

# **SOUTHERN CALIFORNIA PARTICLE SUPERSITE**

**Progress Report for Period May 1, 2001 – August 1, 2001**

**United States Environmental Protection Agency**

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## **1. Introduction**

The overall objective of the Southern California Particle Supersite is to conduct research and monitoring that contributes to a better understanding of the measurement, sources, size distribution, chemical composition and physical state, spatial and temporal variability, and health effects of suspended particulate matter (PM) in the Los Angeles Basin (LAB). The specific research objectives are:

1. To characterize PM, its constituents and precursors, to better understand sources and transport which may affect human exposure and to support development of State Implementation Plans (SIPs).
2. To obtain atmospheric measurements for the support of health studies that are designed to address causal factors, etiologic pathways and mechanisms of PM related morbidity and mortality with particular emphasis on PM source-receptor-exposure-effects pathways.
3. To conduct methods testing that will enable comparisons and evaluation of different technologies for characterizing PM, including evaluation of new instrumentation, sampling methods and federal reference methods.

This report addresses the period from May 1, 2001 through August 1, 2001

## **2. Particulate Sampling at Riverside, and Rubidoux CA**

During this period, we have continued our PM sampling at Riverside, and have deployed the Particle Instrumentation Unit (PIU) to our third Supersite sampling site, in Rubidoux CA, during the 2nd week of June 2001. Sampling at Rubidoux commenced during the last week of June, and continued through September 10, 2001. Our first site, Downey, is considered a “source” site, directly impacted by vehicular emissions by nearby freeways. Our second site, Riverside, is a USC Children’s Health Study site, which the urban aerosol reaches after “maturing” or “aging” for several hours in the atmosphere. Rubidoux is also a receptor site, but although near Riverside, is different in that it is located at the South Coast Air Quality Management District (SCAQMD) station, which is directly downwind of a dairy farm and has been historically high in Ammonium Nitrate. We have continued to conduct side-by-side measurements with SCAQMD to determine the volatile Nitrate losses in their PM<sub>2.5</sub> FRM samples. Additionally, because of the high PM content in Rubidoux, an “intensive” inter-lab comparison study, described below, has been conducted during August 15 through September 8 2001.

During the period covered by this progress report, we have completed most of the chemical speciation analysis for integrated samples collected in Riverside. In addition, we have conducted analyses of the Rubidoux integrated samples, the development of a new high-quality continuous coarse PM monitor, and have begun conducting size-segregated on-line measurements of particulate nitrate using the Integrated Collection and Vaporization System (ICVS) developed by Aerosol Dynamics.

### **2a. Time Integrated Size Fractioned PM Data in Riverside and Rubidoux**

Our current sampling scheme involves the use of three MOUDIs for 24-hour averages: size-fractionated measurements of ambient, and concentrated PM mass and chemical composition. Sampling is conducted once a week, on a Tuesday, Wednesday or Thursday, in order to coincide with one of the sampling days of the AQMD speciation network (which takes place every 3<sup>rd</sup>

day). However, during the August/September “intensive” study, we followed a strict every-third-day integrated filter sampling protocol.

In each run, consistent with our original Supersite proposal, we have used three collocated Micro-Orifice Uniform Deposit Impactors (MOUDI) to group PM into the following size ranges:

- <0.1  $\mu\text{m}$  (ultrafine particles)
- 0.1- 0.32  $\mu\text{m}$  (accumulation mode, “condensation” sub-mode)
- 0.32 -1.0  $\mu\text{m}$  (accumulation mode, “droplet” sub-mode)
- 1.0-2.5  $\mu\text{m}$  (“intermediate” mode)
- 2.5-10  $\mu\text{m}$  (coarse particles)

In addition to mass concentration, the following chemical components have been analyzed within these size groups:

- a. inorganic ions (i.e., sulfate, nitrate, ammonium)
- b. trace elements and metals
- c. elemental and organic carbon (EC/OC) content
- d. concentrations of polycyclic aromatic hydrocarbons (PAH)

Ambient data are averaged over 24 hours, whereas data corresponding to ‘concentrated’ PM are only averaged over two hours, as this is the typical duration of the human exposure experiments, conducted simultaneously with PM sampling.

Due to low relative humidity in ambient air, which creates particle bounce in MOUDI stage 2.5-10  $\mu\text{m}$  and induced potential distorted particle size distribution, a Partisol-Plus sampler (model 2025 Sequential Air Sampler, Rupprecht and Patashnick Co., Inc., Albany, NY) is used to obtain coarse mode (2.5-10  $\mu\text{m}$ ) gravimetric measurement and IC analysis. The Partisol is also used to provide data on mass and chemical composition of coarse (2.5-10  $\mu\text{m}$ ) and fine (PM<sub>2.5</sub>)

in the following time intervals: 6 a.m.-10 a.m., 10 a.m. to 4 p.m., 4 p.m. to 8 p.m. and 8 p.m. to 6 a.m. to investigate the diurnal-pattern changes between locations (e.g., Riverside and Rubidoux).

Sampling has been completed for a total of 17 weeks in Riverside and 11 weeks in Rubidoux. All Riverside samples have been analyzed and only gravimetric measurements are currently available in Rubidoux.

One of the major objectives of the Supersite is to investigate the physiochemical differences between PM source and receptor locations within the Los Angeles basin. Table 1 presents the particle mass concentration size distribution in five PM<sub>10</sub> sub modes for Downey (about 1 mile downwind of the 710 Freeway; i.e., a source site) and Riverside (about 45 miles down wind; i.e., a receptor site). It shows that the mode of the particle mass shifts from the “condensation” sub mode ( $9.29\mu\text{g}/\text{m}^3$ ) in Downey to the “coarse” fraction ( $7.7\mu\text{g}/\text{m}^3$ ) in Riverside. Also, the mass concentration of the condensation sub mode decreases from  $9.3\mu\text{g}/\text{m}^3$  in Downey to  $3.4\mu\text{g}/\text{m}^3$  in Riverside. Normally, “condensation” particle growth occurs rapidly, and Downey is immediately downwind of the 710 Freeway, which has the greatest heavy engine diesel truck traffic density in Los Angeles (about 30 to 40% of total vehicles, at any one time), while the Riverside site does not, and is several miles downwind. Under these conditions, it may be expected that ultrafine particles emitted at the freeway source grow to the droplet sub mode, measured at Downey, while the larger coarse particles at Riverside are from a different sources.

Table 1. PM<sub>10</sub> Mass concentration in 5 sub modes in Downey, Rubidoux, and Riverside

	mass concentration, $\mu\text{g}/\text{M}^3$	
Size, $\mu\text{m}$	Downey*	Riverside**
2.5-10	5.35	7.70
1.0-2.5	3.83	3.61
0.32-1.0	6.81	6.21
0.1-0.32	9.29	3.37
<0.1	3.75	1.57
Total	29.03	22.46

\* Downey: From Oct. 3, 2000 to Feb. 1, 2001, N=13;

\*\* Riverside: From Feb. 21, 2001 to June 6, 2001, N=17

Filter samples are also chemically speciated, in part, to: determine the source receptor trajectory profile, and to provide information for other Supersite related health studies within the SCPCS and for the NARSTO archives. Organic Carbon (OC) is a direct primary emission product from mobile sources, especially diesel. During and immediately after the combustion process, it may act as a nuclei particle (i.e., within the “ultrafine” size range). Semi volatile organic carbon (SVOC) compounds may condense onto the nuclei, thus forming the condensation sub mode. Additional collisions with water molecules and further condensation of SVOCs and water vapor can generate larger particles (i.e., in the “droplet” mode ). Ammonium Nitrate ( $\text{NH}_4\text{NO}_3$ ) associated air pollution particles can be formed by the reaction of Ammonia ( $\text{NH}_3$ ) gas and primary and secondary translocated  $\text{NO}_x$  emissions. They tend to predominate in the 2.5 micro-meter fraction of particulate matter. Figures 1 present MOUDI collected mass concentrations, by chemical group, at both sites. Much higher levels of OC, in the PM10 fraction (about  $16.7 \mu\text{g}/\text{m}^3$ ), have been measured in Downey, compared to about  $5.0 \text{ ug}/\text{M}^3$  in Riverside. In comparison, particulate  $\text{NH}_4\text{NO}_3$  levels are predominantly greater in Riverside ( $8.7 \mu\text{g}/\text{m}^3$ ), then in in Downey ( $4.5 \mu\text{g}/\text{m}^3$ ). The results also show that OC dominates all other chemical species in the PM 2.5 fraction in Downey. At Riverside the total PM10 mass of OC is only 38% of that at Downey. This most likely is due to the lower local diesel vehicles in Riverside. In contrast,  $\text{NH}_4\text{NO}_3$  is about twice as high in Riverside, but dominant in the droplet mode. Riverside is about 10 miles downwind of a large dairy farm (Mira Loma), which under the prevailing metrological conditions of eastern Los Angeles becomes an  $\text{NH}_3$ -gas source. The mobile source Nitrogen Oxide gas emissions are transported across the dairy farm, via a South Westerly “Nitrate Trajectory” (Cass, 1987), and under the intense summer-time photochemical conditions (typically between 90 to 105 degrees F) mix with the  $\text{NH}_3$  to form  $\text{NH}_4\text{NO}_3$  particles at and directly upwind of Riverside.

The contributions of chemical groups to PM10 at our source and receptor sites can also be expressed as a fraction of the total chemical mass for each group (see Figure 2). The relative amounts of a chemical group within a size mode may reflect its source(s). For example,

Elemental Carbon, a mobile source emission, is proportionally greater in the ultrafine mode in Downey (74% of total EC mass concentration), but in Riverside it is evenly distributed in the ultrafine fraction, and condensation and droplet sub modes (between 25 and 35%). This suggests that the EC particles are generated near the 710 Freeway (in this study), measured in the nuclei phase early in their trajectory at Downey, and they then grow by accumulation to form larger particles about 45 miles downwind in Riverside.

Fractionally, metal oxides and elements (P, Br, and Cl) are the major constituents in coarse mode, approximate 75% by mass in 1.0-10 $\mu$ m and do not show quantitative differences in Downey and Riverside (4-5  $\mu$ g/m<sup>3</sup>), which implies the sources of coarse mode particles are mostly generated by local sources as well.

A total of 5 sets of 24 hour time-integrated MOUDI measurements were conducted to investigate particle size distribution in Rubidoux. More than 60% of PM 10 mass is in the size range from 2.5-10 $\mu$ m and the tail of **coarse** particle has extended to 1.0-2.5 $\mu$ m with fraction of 15%. The reason for pronounced **coarse** mode can be explained by the dry and hot meteorological condition in Rubidoux during summer. Detail chemical profiles shall be presented after complete chemical analysis.

## **2b. Size Distribution, Diurnal and Seasonal Trends of Ultrafine Particles in Source and Receptor Sites of the Los Angeles Basin**

In our previous report, we presented our preliminary results on the relationship between hourly ultrafine number and mass concentrations data of a given day to the hourly relationship between the hourly concentrations of EC and PAH measured by the Aethalometer. All of those data were selected from a typical days. We further extended these analyses in a systematic way by averaging all the Monthly data to investigate the generalized temporal trend of ultrafine PM characteristics under the influence of source and receptor sites in Los Angeles air basin. Ultrafine

PM size distributions were analyzed in greater detail to demonstrate the differences between Downey and Riverside.

Hourly number concentrations highly correlate with corresponding ultrafine mass concentrations measured at both sites over the entire time periods as shown in Figure 3. The high correlation ( $R^2 = 0.74$ ) suggests that number concentration can be reasonably good indicator of the ultrafine mass concentration at least in Los Angeles area. In addition, this high degree of correlation precludes homogeneous nucleation from being a significant formation mechanism of ultrafine PM in both sites.

Turpin and Hutzincker (1995) suggested that the significance of secondary organic aerosol atmosphere of Riverside promoting the formation of secondary organic aerosols in addition to the primary organic aerosols. We believe the latter is the actual case at Riverside and further examined the data could be assessed by plotting organic carbon against the elemental carbon concentrations measured in a given locations. As shown in Figure 4a, organic carbon concentrations at Downey strongly correlated ( $R^2 = 0.89$ ) with concentrations of elemental carbon, which (in the absence of wood burning) is a primary tracer of vehicular emission. The average ratio of organic carbon to elemental carbon at Downey, estimated from slope of the linear regression, is 3.5 (equivalent to 2.5 based on unit of  $\mu\text{gC}/\text{m}^3$ ) and very close to the previously reported value for the aerosols at Long Beach (Turpin and Hutzincker, 1995) that is located to the southeast of Downey by about 10 km and considered as a typical source site. Figure 4b shows a rather weak association ( $R^2 = 0.27$ ) between organic carbon concentrations and elemental carbon concentrations at Riverside, indicating that at least a significant portion of organic carbon at Riverside originates from sources that are unrelated to local vehicular emissions. The high average ratio of organic carbon to elemental carbon concentrations (8.6 from the slope of linear regression) also implies the existence of secondary organic aerosols in ultrafine particles at Riverside.

Figures 5 a - c shows the diurnal pattern of ultrafine number concentrations averaged over the month period together with elemental carbon (EC) concentrations as marker of primary combustion source. As seen in Figure 5a in most of time of day, number concentration of ultrafine particles at Downey follows well the elemental carbon concentration, indicating most of

ultrafine particles are associated with primary combustion sources such as vehicular emission. The peaks of both EC and number concentration in morning time (6 to 9 AM local time) are probably due to the local vehicular emissions under the stable atmospheric condition before sea breeze is developed. An increase of number concentration after 6 PM local time may result from a decrease in atmospheric mixing height combined with stagnant condition during the nighttime. At Riverside site, the average number concentration exactly follows the EC trend in February (see Figure 5b) similarly as in Downey site, indicating that ultrafine particles at Riverside in cold season are mostly associated with the local primary combustion sources. However, this strong correlation between number and elemental carbon concentrations does not persist in hot season such as May, especially in the afternoon. As shown in Figure 5c, ultrafine number concentration starts to increase abruptly in the afternoon while elemental carbon concentration gradually decreases. This observation at Riverside in hot season strongly implies the existence of another source for ultrafine particles at elevated temperature (or intensive solar radiation) in the afternoon in addition to preexisting primary emission sources like vehicular emission.

For the better understanding of temporal variation of particle size distributions, geometric mean diameters of particles were averaged over the month as a function of hour of the day. In Figures 6 a and b, the monthly averaged geometric mean diameters in two sites, Downey and Riverside are plotted against time of the day. On average, geometric mean diameters of ultrafine particles in Downey are smaller than 60 nm in most time of the day. We believe that constant traffic on the freeway 710 near the Downey site consistently provides fresh ultrafine particles, therefore maintains the geometric mean diameters below 60 nm. A relatively increased geometric mean diameter during the nighttime, especially in cold season like January and February is presumably driven by growth of hygroscopic aerosols such as ammonium nitrate and ammonium sulfate. Overall, there is no real difference of geometric mean diameters with month in Downey, regardless of hot or cold season. The absence of temporal change in geometric mean diameters reflects that ultrafine particles in Downey site are mostly determined by primary emissions from constant local source such as vehicular exhaust. There exist, however, a distinguishable change in geometric mean diameters at Riverside site as season progresses. Figure 6b illustrates the increasing trend of geometric mean diameters in Riverside from late February to May. This



increase of geometric mean diameters with season at Riverside site is much more pronounced in the early afternoon. These seasonal and diurnal trends of geometric mean diameter in Riverside strongly imply the existence of secondary aerosol formations during the daytime in Riverside in addition to the existing primary emission sources.

Figures 7 and 8 demonstrate the actual size distributions of ultrafine particles selected from typical days measured at two sites, Downey and Riverside. As shown in Figures 7 a-d (10<sup>th</sup> October in 2000), ultrafine particles measured in Downey consist of uni-modal distributions with geometric mean diameters less than 60 nm. Furthermore, there was little variation in geometric mean diameters over 12 hours during the daytime reflecting constant vehicular emissions from nearby freeway at Downey area.

Compared with obvious uni-modal size distributions at Downey, ultrafine particles measured at Riverside show bimodal size distributions as seen in Figures 8 measured on 16<sup>th</sup> May, 2001. In order to distinguish actual contribution from each mode (one mode less than 100 nm and the other larger than 100nm), measured bi-modal size distributions were inverted to sub-modes by means of multi-peak curve fitting assuming log-normal behavior of individual size distribution. Since our primary interest was on the temporal trend of smaller size mode less than 0.1  $\mu\text{m}$ , geometric mean diameter of larger modes were fixed at 164 nm that was first simulated using the specific size distribution at noontime. The larger mode near noontime is relatively bigger than the smaller mode, therefore can serve as a reference peak for the purpose of curve fitting of varying sub-mode less than 0.1  $\mu\text{m}$ . The first thing to notice in Figures 8 a-d is significant portion of sub-mode with geometric mean diameter larger than 0.1  $\mu\text{m}$ , to say, accumulation mode at Riverside. Unlikely Downey site dominated by uni-modal size distribution, Riverside is enriched by particles in accumulation mode as well as ultrafine mode on the basis of “number” concentrations. This coexistence of two modes at Riverside site mostly explains the relatively larger geometric mean diameters at Riverside than Downey as shown in Figures 6. The abundance of particles in accumulation mode well characterizes Riverside as “receptor” site contrasted with Downey site that consists of ultrafine mode only. PM originally emitted in urban Los Angeles is also affected in this area after several hours of suspension in the atmosphere. During the transportation, ultrafine particles grow slowly by coagulation with small

particles and/or by condensation from low vapor phase species and eventually reach the larger particles size. Another interesting feature found in Figures 8 a-d is the evolution of smaller sub-mode (or ultrafine mode) with time in the afternoon. The intensity of smaller sub-mode starts to increase from noontime, reaches maximum at 3-4 PM and reduces after 4 PM. The smaller mode, nucleation mode accounts for 32, 50 and 65 % of the total number counts of entire number size distributions at noon, 2 PM, and 4 PM, respectively (at Riverside on 5/16/2001). We believe this increase of ultrafine peak is due to the heterogeneous nucleation process in site. Nucleation process is the only formation mechanism to increase the number concentration of ambient aerosols among other mechanisms such as coagulation and condensation. Change in the depth of mixing layer can not explain the increase of number concentrations of ultrafine particles since more stable accumulation mode decreases during the corresponding time period.

Regardless of types of nucleation, nucleation process must occur at elevated concentrations in low vapor pressure species. Woo *et al.* (2001) have also reported ultrafine events in the size range of 35-45nm accompanied by elevated gas pollutants including SO<sub>2</sub>, NO, NO<sub>2</sub>, NO<sub>x</sub>, and NO<sub>y</sub>. These gas pollutants from primary emissions can react with other organic compounds to convert condensable low vapor species, preferably by photochemistry under the intensive solar radiation around noontime. Furthermore, the occurrence of heterogeneous nucleation process only at Riverside, a receptor site implies that certain time interval is required for the photochemistry to occur during the transformation of precursors from Downey, a source site to Riverside.

### **3. Evaluation of Nitrate Sampling Artifacts of the FRM in Measuring the True PM<sub>2.5</sub> Concentrations**

These investigations are conducted in collaboration with the South Coast Air Quality Management District (SCAQMD). The research objective of these studies is to determine the degree to which Nitrate (as NH<sub>4</sub>NO<sub>3</sub>) is lost during the 24-hr sampling period from the Teflon filters of the FRM. This study started on March 15, 2001 in Riverside and has continued through,

at least, the end of the summer of 2001 in Rubidoux. At each intensive sampling site, the 24-hour average “actual mass” concentrations for  $PM_{2.5}$  are compared to those obtained with the FRM, of which “actual mass” refers to  $NH_4NO_3$  less the potential positive and negative volatile Nitric Acid ( $HNO_3$ ) artifacts.

The  $PM_{2.5}$  FRM  $NH_4NO_3$  measurements were obtained via a Partisol (Rupprecht & Patashnick, Model 2025). A Harvard Annular Denuder System (HEADS) was used to measure the “actual”  $NH_4NO_3$  mass measurements. A carbonate coated annular denuder of the HEADS efficiently removes ambient  $HNO_3$ -gas that may act as a potential positive artifact on the “actual”  $NH_4NO_3$  highly efficient Nylasorb filters. The Nylasorb filters are used to prevent volatilization of  $NH_4NO_3$ .

Preliminary results are of measurements made at the Riverside site. Figure 9 illustrates that the  $NH_4NO_3$  measured by the Annular Denuder was, on the average,  $6.4 \text{ ug/M}^3$  greater than that measured by the FRM. The HEADS was consistently greater with differences ranging from 1.7 to  $10.7 \text{ ug/M}^3$ , which may be explained by variations in ambient  $HNO_3$ , Temperature, Relative Humidity, and Total PM Mass. Analysis of the effects of these variables will be presented in our next progress report. Additionally, comparisons will be made with the South Coast Air Quality Management Districts’ (SCAQMD) FRM measurements. These analyses will be conducted once our filters are analyzed and data received from the Rubidoux measurements, of which had been conducted between mid June to mid September.

Figure 10 is a scatter plot of particulate  $NH_4NO_3$  and Sulfate (reported as Ammonium Sulfate  $(NH_4)_2SO_4$ ). The correlation coefficients ( $R^2$ ) for the HEADS, as a function of FRM measurements, result in  $R^2$  of 0.95 for  $NH_4NO_3$  and 0.86 for  $(NH_4)_2SO_4$ , respectively. The greater variation in Sulfate measurements may be attributable to the specificity of the HEADS for semi-volatile Nitrate, but not semi-volatile Sulfate. The high correlation for both, especially Nitrate suggests that a great consistency in experimental measurement, and that the differences between the two systems are most likely due to their intrinsic differences rather than error. The slope of the sulfate is nearly one-to-one, and nearly intercepts zero, whereas the measurements by

the HEADS Nitrate was higher by about 7% throughout the range of measurements. This further indicates that the HEADS substantially excludes for artifact Nitrate. Although its denuder removes ambient  $\text{HNO}_3$ , which may result in lower HEADS  $\text{NO}_3$ , the FRM uses a Teflon filter, which does not capture semi-volatile Nitrate. Moreover, thus, this suggests that the loss of Nitrate from the FRM may be as much as 7%, or more.

#### **4. Development of a New High-Quality Continuous Coarse PM Monitor**

##### **INTRODUCTION**

The development of a continuous coarse (2.5 – 10  $\mu\text{m}$ ) particle mass (PM) monitor can provide reliable measurements of the coarse mass (CM) concentrations in time intervals as short as 5-10 minute. The operating principle of the monitor is based on enriching CM concentrations by a factor of about 25 by means of a 2.5  $\mu\text{m}$  cutpoint round nozzle virtual impactor, while maintaining fine mass, i.e., mass of  $\text{PM}_{2.5}$  (FM) at ambient concentrations. The aerosol mixture is subsequently drawn through a standard TEOM, the response of which is dominated by the contributions of the CM, due to concentration enrichment. Findings from the field study ascertain that a TEOM coupled with a  $\text{PM}_{10}$  inlet followed by a 2.5  $\mu\text{m}$  cutpoint round nozzle virtual impactor can be used successfully for continuous CM concentration measurements.

The conventional  $\text{PM}_{10}$  inlets available operate at a flow are of 16.7 L/min. The purpose of this study was to develop and test a  $\text{PM}_{10}$  designed to operate at 50 L/min which could be used for the Continuous Coarse Particle Monitor (CCPM). For this purpose the existing  $\text{PM}_{10}$  inlet operating at 16.7 L/min was modified. The choice of the sampling flows as well as the nozzle design parameters was made so that the predicted cutpoint of the impactor will be about 10  $\mu\text{m}$ .

## **METHODS AND RESULTS**

### **Lab Characterization**

The 50 L/min PM<sub>10</sub> inlet was first tested in the laboratory. Particle penetration through the impactor was measured as a function of particle size by means of a Nephelometer, DataRAM (RAM-1, MIE Inc., Billerica, MA), which was used to measure the mass concentrations of the monodisperse upstream and downstream of the PM<sub>10</sub> inlet. The result of this test are shown in figure 11. As seen from the figure, the particle collection efficiency increases sharply with increase in particle aerodynamic diameter (AD).

### **Wind Tunnel Test**

The PM<sub>10</sub> inlet was tested for collection efficiency at wind velocities of 3 and 8 km/h in a Wind Tunnel facility at UCLA. Three isokinetic samplers operating at 10 L/min were used as reference samplers. Fluorescent particles were generated for various sizes & their penetration was determined as a function of wind velocity. Figure 12 shows the results of these tests. The wind velocity of 0 km/h is taken as laboratory baseline.

### **Field Tests**

The performance of 50 L/min PM<sub>10</sub> inlet was evaluated at Rubidoux, CA. For this purpose, a 2.5 µm, round nozzle virtual impactor was connected right after the PM<sub>10</sub> inlet. Particles smaller than 10 µm in AD are drawn through the virtual impactor, which was designed to have a theoretical 50% cut point at about 2.5 µm for an intake flow rate of 50 L/min. Coarse particles follow the minor flow, while particles smaller than the cutpoint of the virtual impactor follow the major flow. The minor flow in these experiments was set at 2 L/min to achieve a nominal enrichment factor of 25. A 47 mm Teflon filter placed after the virtual impactor collected the enriched mass. The enriched concentration obtained from the PM<sub>10</sub> inlet was compared to co-located Dichotomous Partisol-Plus (Model 2025 Sequential Air Sampler, Rupprecht and Patashnick Co. Inc., Albany, NY). The Partisol uses a PM<sub>10</sub> inlet operating at 16.7 L/min to remove particles larger than 10 µm in AD. Two separate flow controllers maintain the coarse mass at 1.67 L/min and the fine mass stream at 15 L/min. Coarse & fine mass are collected on two 4.7cm Teflon filters, placed in the minor and major flows of the Partisol virtual impactor, which are housed in

reusable cassettes. Figure 13 shows the comparison between coarse concentrations between the PM<sub>10</sub> inlet & the Partisol. As seen, a very high correlation coefficient of 0.9255 persists between the concentrations.

## **CONCLUSION**

Based on these results, it can be ascertained that the redesigned PM<sub>10</sub> inlet operates successfully at 50 L/min and can be coupled & operated with the CCPM. More tests based on chemical analysis can be performed to corroborate the effectiveness of the inlet.

## **5. Development of a Method for Size-dependent Chemical Composition of Ultrafine Particles (Nano-MOUDI)**

### **Introduction**

Ultrafine particulate matter (PM) consists of particles mostly emitted by combustion sources as well as formed during gas-to-particle formation processes in the atmosphere. Various studies have shown these particles to be toxic. Because of their lack of mass, these particles have been impossible to collect in measurable amounts over practical time intervals. The very small mass of these particles has also posed a great challenge in determining their size-dependent chemical composition using conventional aerosol sampling technologies. Implementing two technologies in series has made it possible to overcome these two problems. The first technology is the USC Ultrafine Concentrator, which concentrates ultrafine particles (i.e., 10-180 nm) by a factor of 20-22. Ultrafine particles are subsequently size-fractionated and collected on suitable substrates using the NanoMOUDI. The NanoMOUDI is a recently developed cascade impactor that utilizes micro-orifice nozzles operating at low pressures to classify particles in 5 size ranges from 10 to 180 nanometers.

The entire system (concentrator + NanoMOUDI) was characterized in the laboratory where local ambient concentration levels were shown to be enriched via the concentrator by a factor of 20. The system was then employed in the field at two different locations in the Los Angeles Basin in order to collect the ultrafine particles in three consecutive 3-hour time intervals

(i.e., morning, midday and afternoon). The filters were then weighed and analyzed for elemental and organic carbon, nitrate, and sulfate. Results on the size distribution as well as the chemical constituents of each range are presented in this paper.

## **Downey**

Figure 14 presents the variation of daytime ultrafine mass concentrations at Downey, separately, for the morning, midday, and afternoon periods. The combination of increasing wind velocity and atmospheric mixing depth most likely cause the decrease in mass concentrations of all species throughout the day. All three time intervals are driven by the organic carbon size distribution because Downey is a “source” site. The size distribution of elemental carbon closely follows that of the total mass with the most deviation occurring in the morning, when the primary sources of elemental carbon presumably contribute the most. Elemental carbon is abundant in the morning, which most likely occurs due to the combined effects of overnight and early morning accumulation of the emissions from the steady truck traffic and the depressed atmospheric mixing depth.

The amount of particle-bound nitrate in Downey decreases all through the day. As with the other chemical constituents and the total mass distributions, a minimum can be observed in the 56-100 nm range. Nitrate is probably decreasing throughout the day due to the increasing temperature and decreasing relative humidity, both of which cause the particle-gas phase nitrate equilibrium to shift from the particulate to gaseous form (Mozurkewich, 1993).

Ultrafine PM sulfate displays a bi-modal distribution, with measurable amounts in the 32-56 and 100-180 nm ranges. The 32-56 nm mode originates probably from sulfur contained in diesel vehicular emissions, as discussed in the previous paragraph, whereas the 100-180 nm is mostly generated by photochemical oxidation of sulfur dioxide (SO<sub>2</sub>) to sulfate during midday and afternoon. These two different formation mechanisms may explain the decrease of sulfate in the 32-56 nm mode (i.e., the decrease in traffic and increase in atmospheric mixing depth) and the increases in the 100-180 nm modes as the day progresses

## **Riverside**

Figure 15 presents the variation of daytime ultrafine mass concentrations at Downey, separately, for the morning, midday, and afternoon periods. Because Riverside is a receptor site, the highest mass concentrations are found in the afternoon while midday concentrations are the lowest. The decline at midday is most likely due to a combination of increasing wind velocity and mixing depth as the day progresses. The afternoon concentrations, however, peak because of secondary particle formation through photochemical reactions, occurring during the warmest part of the day (Pandis et al., 1992). While the morning and midday size distributions remain fairly constant, with mass concentration decreasing with time, the afternoon distribution differs from these in both shape and intensity.

The organic carbon size distribution is very similar to that of total mass; as with Downey, organic carbon is the predominant chemical constituent of ultrafine PM at Riverside, accounting for approximately 50-80% of the total mass. Elemental carbon concentrations are very small in the ultrafine mode for all time periods at Riverside, which demonstrates the lack of overnight and morning diesel emissions in that location compared with Downey. Vehicular emissions are still the main sources of EC found in ultrafine PM at Riverside, but the lower concentrations are due to the overall lower traffic in that region compared to that of downtown Los Angeles.

Further evidence of increased secondary aerosol formation in the Riverside area compared to Downey is provided by examining the diurnal trends in the concentrations of particulate-bound nitrate. Particulate nitrate in Riverside is almost exclusively found in particles larger than 100 nm, and its concentrations increase throughout the day, which is exactly the opposite trend of that in Downey. Unlike Downey, Riverside is located a few kilometers downwind of major ammonia sources generated by local agriculture and dairy farms (Kleeman et al., 1999).

The particle-bound sulfate concentrations increase from morning to afternoon similarly to the particulate nitrate concentrations. Similar to the results observed in Downey, small but measurable amounts of sulfate were found in the 32-56 nm mode. Given that the concentrations in this sub-mode increase as the day progresses (and opposite to Downey), we hypothesize that they probably originate from diesel emissions from the urban areas of Los Angeles, especially



given the lack of sulfate emissions in Riverside (Kim et al., 2000). The majority of sulfate was found in the 100-180 nm range, hence the “tail” of the accumulation PM mode.

## SUMMARY AND CONCLUSIONS

This study demonstrates the use of a technology that can collect size-segregated, ambient ultrafine particulate matter on substrates that can be further analyzed for chemical speciation. By concentrating ambient ultrafine aerosols at two locations in southern California before entering a cascade impactor under vacuum, measurable mass can be obtained for time periods on the order of 3 hours. Because of the localization of ultrafine PM and brevity of events and mechanisms that might be responsible for its formation, sampling over shortened intervals has greater practicality than the traditional 24-hour sampling experiments. Although the results presented in this paper provide new insight into ultrafine PM formation mechanisms in locations of the Los Angeles Basin that are impacted by either primary or secondary aerosol formation processes, they are not intended to comprehensively explain ultrafine PM and its characteristics. This technology can, however, be duplicated at various locations and times in order to develop a comprehensive understanding of the formation mechanisms, transport and transformations of ultrafine particles.

The ultrafine aerosol concentration enrichment by a factor of over twenty allowed size-fractionated collection of weighable and analyzable amounts of ultrafine PM in five ranges from 10 to 180 nm in 3 hour sampling periods. Despite the rather limited number of sampling days, substantially different trends in the size distributions and diurnal trends for mass and chemical constituents were observed between the two sampling sites, thereby providing insights on differences in the ultrafine particle formation processes in each location. At Downey, a “source” site, impacted primarily by vehicular emissions of nearby freeways, very strong correlations were obtained for particulate elemental versus organic carbon throughout the day. In Riverside, a “receptor” site in the Los Angeles Basin, ultrafine EC and OC concentrations were highly correlated only during the morning period, whereas these correlations collapsed later in the day. These results indicate that in this area, ultrafine PM are generated by primary emissions during

the morning hours, whereas secondary aerosol formation processes become more important as they day progresses.

## **6. Size-segregated on-line measurement of particulate carbon and nitrate using the Integrated Collection and Vaporization System**

### Current Progress

During this quarter, we completed laboratory testing on a cascaded Integrated Collection and Vaporization System (ICVS) system for particulate nitrate, and installed the system in the UCLA/USC mobile laboratory. Field operations began at the Rubidoux field site on July 12, 2001.

The cascaded ICVS consists of three stages, designated “A”, “B”, and “C”, as shown in Figure 16. After passing through a 2.5  $\mu\text{m}$  precut the sample is humidified to 65% relative humidity (RH) using a nafion-based humidity conditioner. A target of 65% RH was chosen to allow for enough humidification of the aerosol to prevent bounce, but not so much as to drastically increase particle size. Particles below the 2.5  $\mu\text{m}$  precut and above 1.0  $\mu\text{m}$  aerodynamic diameter at 65%RH are collected in Stage A ( $D_{\text{jet}}=0.039\text{in}$ ). The humidity is not changed through Stage B, which collects particles above 0.45  $\mu\text{m}$  aerodynamic diameter ( $D_{\text{jet}}=0.024\text{in}$ ). The sample then passes through a nafion humidifier with a liquid water sheath to achieve humidity above 90% before impacting Stage C ( $D_{\text{jet}}=0.0145\text{in}$ ). Stage C collects particles above 0.14  $\mu\text{m}$  with an efficiency of 95% or greater.

Results of laboratory testing for size differentiation for the cascaded system are shown in Figure 17. Data were collected by supplying the cascaded ICVS with ammonium nitrate aerosol generated by our high flow differential mobility analyzer (HF-DMA). A single-jet impactor with an appropriate size cut upstream of the HF-DMA served to remove the larger, doubly-charged particles, whenever possible. When this was not possible for specific particle sizes, data were corrected for the presence of doublets based on size-distribution data from an optical particle

counter run in parallel with the ICVS. Data collected at  $0.19\text{ }\mu\text{m}$  show a doublet at  $0.30\text{ }\mu\text{m}$  that could not be differentiated from the OPC data, skewing the results toward Stage B.

The data in Figure 17 are plotted as a function of the Stokes diameter for dry ammonium nitrate, as sized by the HF-DMA. The sizing of the cascaded ICVS is for these same particles humidified to 65% RH. Stage A collects particles in the range  $0.95\text{--}2.5\text{ }\mu\text{m}$ , Stage B  $0.4\text{--}0.95\text{ }\mu\text{m}$ , and Stage C collect particles smaller than  $0.4\text{ }\mu\text{m}$  (Stokes diameters). These sizes confirm good differentiation of the ambient aerosol modes discussed in the previous report. Stage A corresponds to the coarse mode, Stage B to the droplet mode, and Stage C to the condensation mode and a portion of the nuclei mode.

Some representative field data are displayed in Figures 18 and 19. Diurnal peaks in total nitrate are observed near 12:00 daily with occasional smaller increases in the early morning hours. It is interesting to note that Stage C, the smallest size range, often increases first, followed by the larger Stages A and B one to three hours later. The Mass Mean Diameter is a mass weighted average based on the geometric mean of the particle size range for each stage and shows the changing distribution of mass over the size spectrum. The mass balance shifts toward larger particles immediately following a peak in total nitrate mass. These preliminary analyses point to the potential of this system for understanding atmospheric particulate nitrate formation mechanisms.

### Upcoming Work

Work is continuing to perfect the humidity control system for Stages A and B. The humidity remains within 1% of the target for all periods except when the ambient relative humidity drops below approximately 25%. At very low ambient humidity the controlled humidity in Stages A and B has dropped as low as 42%, with regular drops to 50%. We have observed a daily drop in the controlled humidity during periods from 12:00 to 18:00 hours.

The saturated air used for the humidity system is produced at the temperature of the air-conditioned trailer before entering the instrument enclosure, which is maintained at close to the much warmer ambient temperature. Therefore, the air is no longer saturated when it enters the annular sheath of the nafion tube, losing some ability to humidify the aerosol. Efforts are underway to mount the humidification bottle inside the instrument enclosure to prevent this problem. These modifications will be incorporated into the forthcoming particulate carbon system.

The size-segregated ICVS particulate carbon system has been constructed very similarly to the nitrate system and will undergo lab testing in the coming weeks. Plans are to install the carbon system in the mobile laboratory when it is transferred to the next sampling site. At that time the nitrate humidity control system will be updated as well.

## **7. Sampling and Determination of Ambient Levels of PAHs, Quinones, Carbonyls, EC and OC in CHS Sites. Phase I: Atascadero, San Dimas, and Riverside**

### **7a. Summary of Activities and objectives**

During the reporting period, the SCPCS Chemical Analysis Laboratory (CAL) provided analytical core support for several SCPCS investigators. One major effort of our laboratory activities during the period was directed towards the determination of gas- and particle-phase PAHs and quinones, EC and OC, and carbonyls present in ambient air in three Children's Health Study (CHS) sites: Atascadero, San Dimas, and Riverside. The major objective of this component of the study is to assess the inter-community variability of ambient levels of polycyclic aromatic hydrocarbons (PAHs), quinones and carbonyls. The study is being performed at sampling locations within the twelve Southern California communities participating in the California Air Resources Board CARB-sponsored CHS, a longitudinal respiratory health study of several thousand Southern California school children.

The objective of the study is to understand seasonal variability and annual levels of organic compounds in the ambient air in the twelve CHS communities which include: Atascadero, Santa Maria, Lompoc, Lancaster, Long Beach, San Dimas, Upland, Mira Loma, Riverside, Lake Arrowhead, Lake Elsinore, and Alpine. Upon completion of about two months' elapsed time, the samplers will be relocated to a second set of three study communities. The samplers will be systematically switched and shared between the two sets of sampling sites, so that during the course of a twelve-month period, information will be available regarding seasonal variation at six sites. On the following twelve-month period, sampling will be conducted at a different set of CHS sites so that, after a two-year period, information on the levels of organics will be available for all twelve CHS sites.

The sampling protocols and the analytical procedures followed have been described in previous reports. Quinone results were not available at the time of this report and will be included in the next quarterly report. At this time, the limited data set available does not allow yet an evaluation of seasonal variability in the concentration of the target species. For this reason, discussion of results for all chemical species measured will be brief.

#### 7b. Chemical Analysis Results and Discussion

Samples were collected during 24 hrs, from 12 am to 12 pm, from May 31 to July 15, 2001, in three CHS sites: Atascadero (ATA), San Dimas (SD) and Riverside (RIV). Due to long travel time between ATA and the other sites, only in SD and RIV samples were collected in the same days and time periods; sample collection in RIV was shifted by a couple of days. The target species determined, their codes and MW are listed in Tables 2 and 3.

**Table 2. Target PAHs, Codes, and MW.**

	<b>PAH</b>	<b>Code</b>	<b>MW</b>
<b>1</b>	<b>Naphthalene</b>	<b>NAP</b>	<b>128</b>
<b>2</b>	<b>Acenaphthene</b>	<b>ACE</b>	<b>154</b>
<b>3</b>	<b>Fluorine</b>	<b>FLU</b>	<b>166</b>
<b>4</b>	<b>Phenanthrene</b>	<b>PHE</b>	<b>178</b>
<b>5</b>	<b>Anthracene</b>	<b>ANT</b>	<b>178</b>
<b>6</b>	<b>Fluoranthene</b>	<b>FLT</b>	<b>202</b>
<b>7</b>	<b>Pyrene</b>	<b>PYR</b>	<b>202</b>
<b>8</b>	<b>benzo(a)anthracene</b>	<b>BAA</b>	<b>228</b>
<b>9</b>	<b>Chrysene</b>	<b>CRY</b>	<b>228</b>
<b>10</b>	<b>benzo(b)fluoranthene</b>	<b>BBF</b>	<b>252</b>
<b>11</b>	<b>benzo(k)fluoranthene</b>	<b>BKF</b>	<b>252</b>
<b>12</b>	<b>benzo(a)pyrene</b>	<b>BAP</b>	<b>252</b>
<b>13</b>	<b>indeno(1,2,3-cd)pyrene</b>	<b>IND</b>	<b>276</b>
<b>14</b>	<b>dibenz(a,h)anthracene</b>	<b>DBA</b>	<b>278</b>
<b>15</b>	<b>benzo(ghi)perylene</b>	<b>BGP</b>	<b>276</b>

**Table 3. Target PAHs , Codes and MW.**

<b>Carbonyl</b>	<b>Code</b>	<b>MW</b>
<b>formaldehyde</b>	<b>FOR</b>	<b>30.03</b>
<b>acetaldehyde</b>	<b>ACD</b>	<b>44.05</b>
<b>acetone</b>	<b>ACE</b>	<b>58.08</b>
<b>acrolein</b>	<b>ACR</b>	<b>56.06</b>
<b>propionaldehyde</b>	<b>PRO</b>	<b>58.08</b>
<b>crotonaldehyde</b>	<b>CRO</b>	<b>70.09</b>
<b>2-butanone</b>	<b>BUT</b>	<b>72.11</b>
<b>methacrolein</b>	<b>MET</b>	<b>70.09</b>
<b>n-butyraldehyde</b>	<b>BUD</b>	<b>72.11</b>
<b>benzaldehyde</b>	<b>BEN</b>	<b>106.12</b>
<b>valeraldehyde</b>	<b>VAL</b>	<b>86.13</b>
<b>m-tolualdehyde</b>	<b>MTO</b>	<b>120.15</b>
<b>hexanal</b>	<b>HEX</b>	<b>100.16</b>

### PAH Concentrations

Samples for PAH/quinone determination were collected during 24 hrs at 113 L/min in ATA (5 samples), SD (6 samples) and RIV (6 samples). For these sites, fifteen target PAHs were quantified. The concentration means for the target PAHs for each of the three sites are shown in Figures 20-22. For clarity, naphthalene (NAP) levels are shown separately in Figure 20; ACE, FLU, PHE and FLT in Figure 21, and ANT, PYR, BAA, CRY, BBF, BKF, BAP, DBA, BGP and IND in Figure 22.

For all samples, the concentration of naphthalene was an order of magnitude higher than that of other semivolatile target PAHs, ranging from 86 to 650 ng/m<sup>3</sup> for individual samples. The mean NAP concentration for ATA (n=3) was lower than for SD and RIV (Figure 20), suggesting a smaller impact of NAP vehicular emissions at this site. The mean concentration of other PAHs were generally higher in SD and RIV than RIV (Figures 21 and 22). The highest mean concentration of other semivolatile PAHs, 14.3 ng/m<sup>3</sup>, was found for PHE in San Dimas (Figure 21). Among the PAHs found predominately in the particle-phase, including BBF, BKF, BAP, DBA, BGP AND IND, benzo(g,h,i)perylene (BGP) showed the highest mean concentration at 0.24 ng/m<sup>3</sup> (Figure 22).

### Carbonyl Concentrations

Samples for carbonyl determinations were collected for 24 hrs at ~125 mL/min and allowed the determination of 13 target carbonyls in ATA (5 samples), SD (6 samples) and RIV (6 samples). Mean carbonyls concentrations found in Atascadero were a little lower than those found in either San Dimas or Riverside (Figures 23-25). Due to the chemical instability of the acrolein component, values for this carbonyl should be considered as “lower limit”.

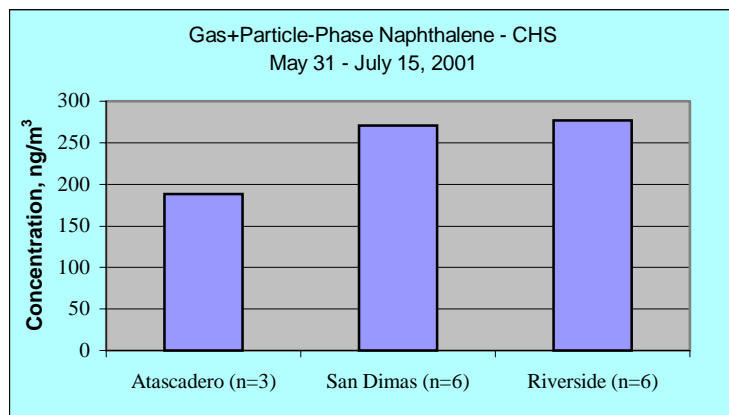
For the three sites studied, the highest mean concentrations found were those of formaldehyde, acetaldehyde, acetone and benzaldehyde, ranging from about 0.65 to 1.4 ppbv. The mean

concentrations of the other carbonyls varied from about 0.01 to 0.2 ppb. Although this limited carbonyl data set does not yet allow an evaluation of seasonal trends, it is note worth noting that similar carbonyls profiles were found at all three sites.

### EC and OC Concentrations

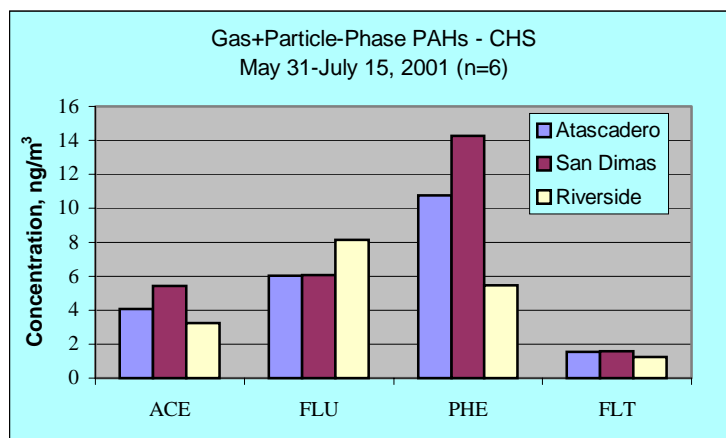
Organic (OC) and elemental carbon (EC) particles constitute a large fraction of the fine PM<sub>2.5</sub> mass in the atmosphere. While fine EC is only produced in combustion processes and is not reactive in the atmosphere, OC is emitted from a number of combustion sources including fugitive area-sources, certain industrial and commercial activities, and as a result of gas-to-particle process that occur in the atmosphere during transport.

EC and OC levels were determined in the same quartz filters used to collect PM<sub>2.5</sub> PAHs. Mean EC and OC concentrations found at the three sites are shown in Figures 26-28. The mean OC concentrations at both San Dimas and Riverside were about 4 times higher than in Atascadero. Mean EC concentrations found in San Dimas and Riverside were respectively, 5.7 and 5.4 times higher than in Atascadero. Because EC concentrations are strongly influenced by diesel engine exhaust emissions, it appears that the Atascadero site is not as strongly affected by direct diesel emissions as the San Dimas and Riverside sites. Again, the limited data set available for EC and OC precludes an evaluation of their seasonal variability.

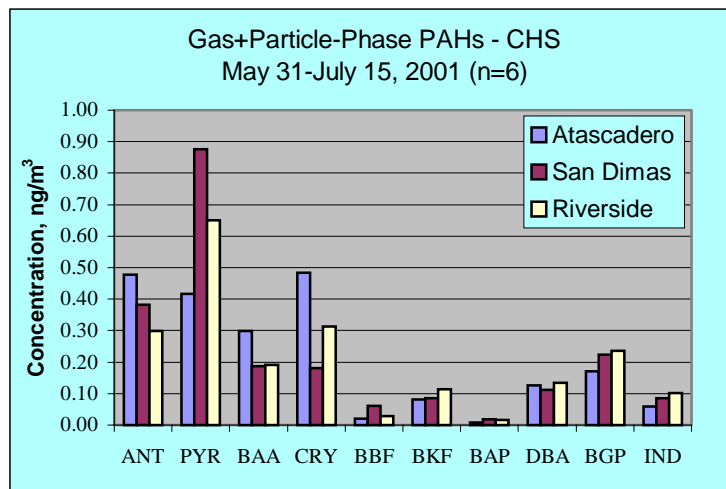




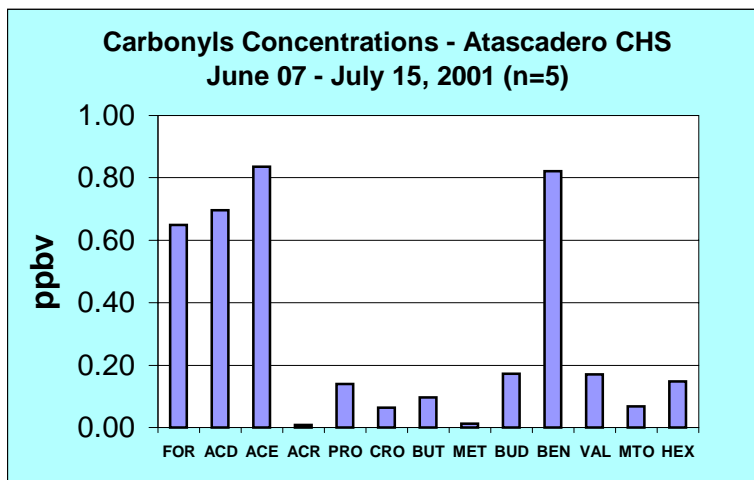
**Figure 20. Mean concentrations of gas+particle phase NAP concentrations for Atascadero San Dimas and Riverside.**



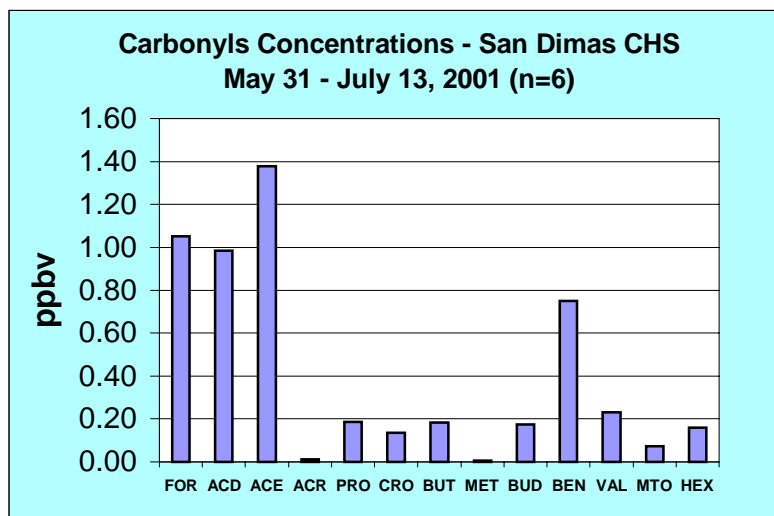
**Figure 21. Mean concentrations of gas+particle phase ACE, FLU, PHE and FLT concentrations for Atascadero (n=5), San Dimas and Riverside (n=6).**



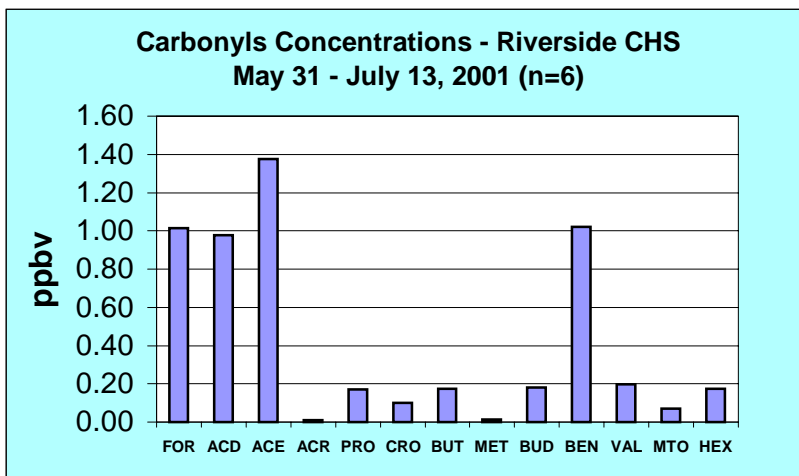
**Figure 22. Mean concentrations of gas+particle phase ANT, PYR, BAA, CRY, BBF, BKF, BAP, DBA, BGP and IND for Atascadero (n=5), San Dimas and Riverside (n=6).**



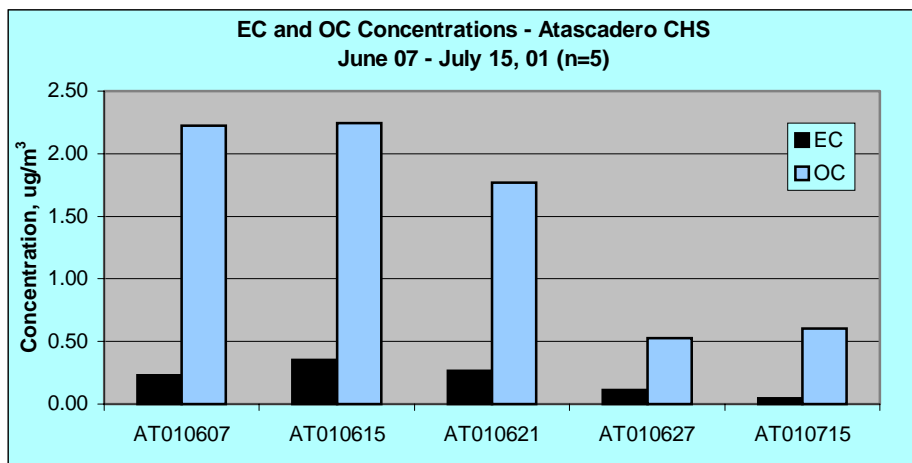
**Figure 23. Mean concentrations of 13 carbonyls for Atascadero.**



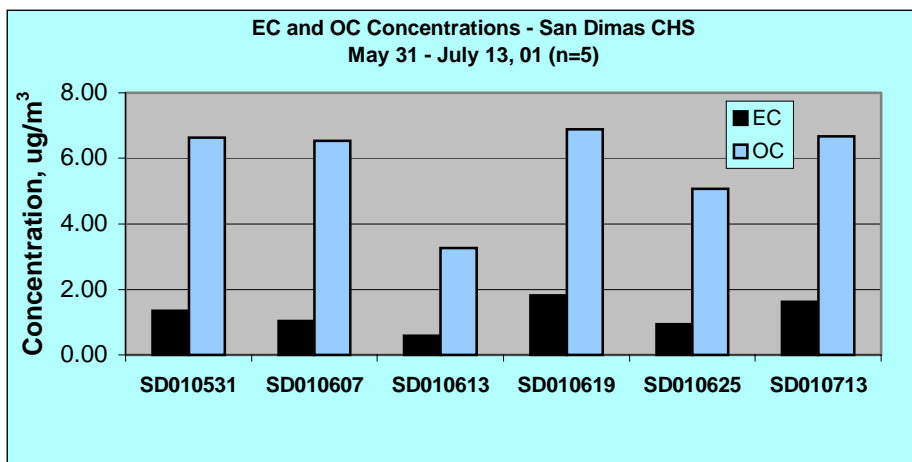
**Figure 24. Mean concentrations of 13 carbonyls for San Dimas.**



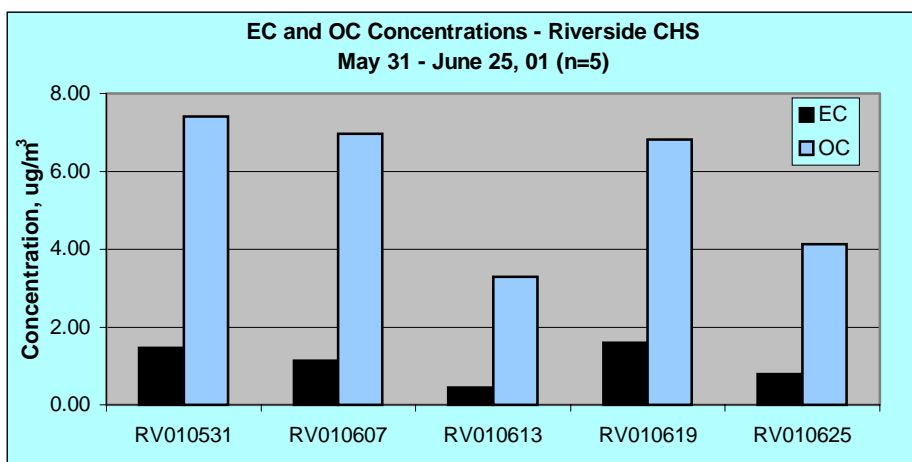
**Figure 25. Mean concentrations of 13 carbonyls for Riverside.**



**Figure 26. Mean concentrations of EC and OC for Atascadero.**



**Figure 27. Mean concentrations of EC and OC for San Dimas.**



**Figure 28. Mean concentrations of EC and OC for Riverside.**

## **8. Characterization of PAH and PAH-Derivatives measured with Hi-Vol**

### Introduction

The goal of our sampling is to characterize the polycyclic aromatic hydrocarbons (PAH) and PAH-derivatives present at sites chosen to represent source sites or downwind receptor sites and to investigate the atmospheric chemistry occurring at these sites during different seasons. Three types of samples are taken to span the range of volatility of the PAH and derivatives: Tenax samples for gas-phase PAH, polyurethane foam (PUF) samples for semi-volatile PAH and nitro-PAH, and Hi-vol filter samples for particle-associated species.

### Downey, CA

Downey, CA is a source site heavily impacted by vehicle emissions. To characterize the Downey site, eight 12-hr daytime and eight 12-hr nighttime samples were collected between November, 2000 and January, 2001. Examining the relationship between the night/day ratios of the individual PAH and their hydroxyl radical rate constants, it was concluded that little daytime hydroxyl radical reaction occurred in these winter samples.

Particulate samples collected at Rancho Los Amigos Hospital in Downey have now been extracted and are being prepared for gas chromatography/mass spectrometry (GC/MS) analysis for

nitro-PAH. An exploratory analysis of one of the Downey particulate samples was made to determine approximate concentrations of 1-nitropyrene and 2-nitrofluoranthene and to determine appropriate concentrations of deuterated nitro-PAH internal standards for the present analysis. The low levels of these compounds found in the exploratory sample indicated that a compositing of three particulate samples would be necessary. Three 12-hour daytime samples (0700-1900 hours) were composited to yield one daytime sample and the three corresponding night samples (1900-0700 hours) were composited to yield one nighttime sample. Table 4, below, shows the compositing method and the air sampling volumes for the samples.

**Table 4.** Compositing method and the air sampling volume.

Sample (Total volume)	Date Sampled	Time Sampled (PST)	Volume (m <sup>3</sup> )
Day (1224 m <sup>3</sup> )	11/2/00	0700-1900	408
	11/30/00	0700-1900	408
	1/4/01	0700-1900	408
Night (1201 m <sup>3</sup> )	11/2-3/00	1914-0700	400
	11/30-12/01/00	1912-0700	401
	1/4-5/01	1910-0700	400

Each of the six 8" x 10" teflon-impregnated glass fiber filter samples was spiked with the deuterated internal standards 1-nitropyrene-d<sub>9</sub> (50 ng) and 2-nitrofluoranthene-d<sub>9</sub> (250 ng) and placed in a Soxhlet apparatus and extracted for 20 hr with 200 ml dichloromethane (DCM). Each of the six extracts was reduced to 2 ml in a rotary evaporator, filtered (0.2μ), and reduced to 100 μl in a gentle stream of dry nitrogen. Each extract will be separated by normal phase high performance liquid chromatography (HPLC) on a silica column (250 x 10 mm, 5μ silica, Regis Chemical Company). The HPLC mobile phase program is as follows: 0-10 min--Hexane; 10-15 min 95% hexane, 5% DCM; 15-40 min--linear gradient to DCM; 40-50 min--DCM; 50-60 min--linear gradient to acetonitrile; 60-70 min--acetonitrile). The nitro-PAH fractions (24-37 min) will

be composited as noted in Table 4 and reduced by rotary evaporation to 1 ml and under nitrogen to 50  $\mu$ l prior to GC/MS analysis.

#### Riverside, CA

As occurred at Downey, CA during the winter months, Tenax TA cartridges were used for ambient air sampling of the gas-phase alkylnaphthalenes. The cartridges (80 mm x 4 mm i.d. Pyrex tubes) were packed with 0.1 g pre-cleaned Tenax TA and were thermally desorbed at 350°C for several hours under helium flow prior to sampling.

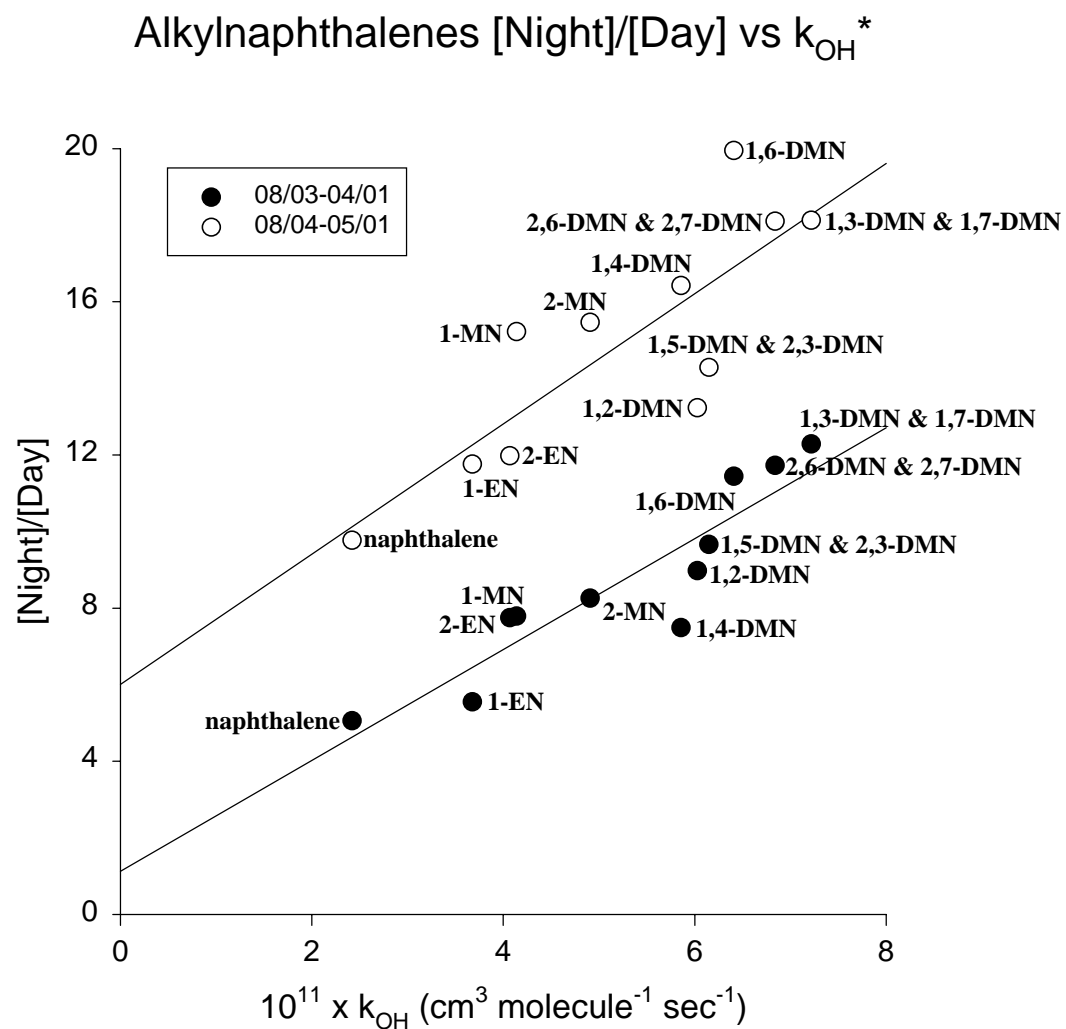
After failing to observe any indication of OH radical-initiated chemistry in several daytime and nighttime samples, we decided to sample only on days with significant ozone and to take 8-hour samples from 1100-1900 hrs to sample reacted vehicle emissions (including emissions transported from the west) and 2300-0700 hrs to collect fresh emissions and/or emissions transported during the nighttime. Tenax samples were collected in Riverside on 08/03-04/01 and 08/04-05/01 from 1100-1900 hrs and 2300-0700 hrs, at a flow rate of 250 ml min<sup>-1</sup>. The O<sub>3</sub> profile on these days resulted in O<sub>3</sub> highs of ~70 ppbv on Friday, 08/03/01, and 140 ppbv on Saturday, 08/04/01 with the ozone remaining elevated for 4-5 hours (~1400-1900 hrs). After sample collection, the Tenax TA cartridges were sealed with Swagelocks and stored in a glass jar and kept cool until analysis.

The alkylnaphthalenes were identified by GC/MS with selected ion monitoring (SIM). Samples were thermally desorbed at 280 °C onto a 60 m DB-1701 column held at 35°C for 10 minutes and then temperature programmed to 100°C at 10°C min<sup>-1</sup>, then to 200°C at 2°C min<sup>-1</sup> and then to 280°C at 20°C min<sup>-1</sup>.

Additional rate constant data for the hydroxy (OH) radical-initiated reactions of C<sub>2</sub>-naphthalenes have been recently obtained and were used to investigate the extent of OH radical chemistry occurring in the Riverside samples. Figure 29, below, shows the results for both night - day sampling pairs. The slope of the [night]/[day] vs k<sub>OH</sub> for the two night - day pairs was quite similar, indicating similar extents of OH radical reaction while the intercept suggests that dilution was more important for the 8/4-5/01 sample.

During August and early September, the daily ozone profiles will be monitored via the South Coast Air Quality Management District website and nighttime sampling will be conducted when the afternoon ozone reaches ~150 ppbv. Sampling will be by polyurethane foam (PUF) plugs in modified Hi-Vol samplers and using a "MegaSampler" equivalent to 16 Hi-Vol samplers that is set up at Riverside. The MegaSampler has been modified by researchers at the Desert Research Institute with 2.5  $\mu\text{m}$  cutoff impactors. The hope is to identify air samples modified by evening nitrate radical chemistry as evidenced from the profile of the methylnitronaphthalenes measured on the PUF plugs. The corresponding filter particle samples will then be analyzed for nitro-PAH, including 2-nitrofluoranthene and nitrobenzanthrones.

Figure 29. Hydroxy (OH) radical chemistry occurring in Riverside for both night and day sampling pairs, includes (OH) radical-initiated reactions of C<sub>2</sub>-naphthalenes.



\* For points representing more than 1 compound, an average  $k_{OH}$  was used.



## 9. Size Distribution And Diurnal Characteristics Of Particle-Bound Metals In Source And Receptor Sites Of The Los Angeles Basin

### *Size Distributions*

The fractional distribution of selected metals and elements in 5 particle size ranges at Downey and Riverside are shown in Figures 30a and 30b, respectively. The values plotted represent 24-hour mass concentration averages of these species in the five PM<sub>10</sub> sub-modes at the two sites. An interesting point that emerges from data plotted in Figure 30 is that unlike Downey, Riverside has a relatively higher fraction of the 2.5-10  $\mu\text{m}$  as opposed to 1-2.5  $\mu\text{m}$  particles for most metals. The relatively coarser metal distributions at Riverside could be explained by examining the average wind speeds at the two locations. Higher wind speeds at Riverside (Figure 35) as compared to Downey (Figure 34) result in formation of more coarse particles, which are primarily produced by wind resuspension. Additionally, Riverside is closer to the Southern California deserts, areas in which coarse particles account for the majority of ambient PM<sub>10</sub> (Ostro et al., 1999; Geller et al, 2001). All these facts explain the relatively coarser metal distributions in Riverside.

The main emission sources of crustal metals seem to be resuspension of dust at both sites. Owing to higher wind speeds at Riverside, their concentrations are much higher at Riverside than in Downey (Figures 31a and 31b). In Downey, crustal metals such as Al, Si, Ca, K and Na are almost exclusively partitioned in the super micrometer size range, with about 60-80% by mass found in the coarse mode and about 15-30% of the total PM<sub>10</sub> mass in the intermediate mode. A second group of metals, such as Fe and Ti display similar size distributions, with the majority of the PM mass in the 1-2.5  $\mu\text{m}$  mode (roughly 40%) in addition to a substantial fraction (around 30%) in the coarse PM mode. The size distributions of these two metals suggest that although technically over 70% of PM<sub>10</sub> by mass can be found in PM<sub>2.5</sub>, similar to the crustals, resuspension of soil and road dust is a significant source of these metals. In Riverside, elements like Al, Si, K, Ca, Fe and Ti are primarily present in coarse particles with percentages varying from 80-90%, thereby suggesting resuspension of windblown dust as the most significant source of these metals. Although relatively lower percentage of Mg (57% by mass) is present in the

coarse mode, about 80% of its total PM<sub>10</sub> mass reside in supermicrometer particles. This size distribution suggests that resuspension of soil dust is the main Mg emission source in Riverside. In contrast, about 40% of manganese Downey is found in the 0.35-1.0  $\mu\text{m}$  range, with the remaining 60% of the mass distributed relatively equally in larger and smaller particles, thereby indicating that the emission sources are split between fuel-oil combustion and soil-or-road dust resuspension.

In Downey, a group of metals viz. Pb, Sn, Ni, and V are present in higher percentages in the finer particles of the accumulation mode and the ultrafine modes. Approximately 70 to 85% of these metals are associated with sub-micrometer particles, and over 40% of the mass concentrations of these metals are associated with particles smaller than 0.35  $\mu\text{m}$ . This suggests that these species originate from anthropogenic sources, such as traffic and industrial emissions, since combustion processes contribute to the formation of small particles. In Riverside, size distributions of Pb and Sn are quite similar, with more than 50% of each associated with PM<sub>2.5</sub> and around 40% present in particles less than 1.0  $\mu\text{m}$ . Ni and V are also associated largely (75 and 65% by mass respectively) with PM 2.5. 67% and 52% by mass of Ni and V respectively are present in finer particles of size less than 1.0  $\mu\text{m}$ . The size distribution of these metals suggests anthropogenic sources like vehicular emissions or other combustion sources as their probable emission sources at Riverside. The concentrations of metals associated largely with fine particles like are much lower in Riverside than in Downey (Figures 32a and 32b). The sampling site in Riverside is upwind of the surrounding freeways and in the absence of any immediate vehicular emission sources their contribution to fine particles is minimal. Fine PM at Riverside consists of particles generated by secondary photochemical reactions as well as those that reach this area, originally emitted in central Los Angeles, after aging for several hours in the atmosphere (Pandis et al., 1992). Due to dispersion in atmosphere, the plume that reaches Riverside is considerably diluted.

### ***Diurnal Patterns***

In the previous report, diurnal trends in the concentrations of metals in the fine and coarse PM modes for the data generated in Downey were discussed. Similar investigations have been

carried out for Riverside. The results are summarized in Figure 33. The diurnal trends in the concentrations of each metal are quite similar. In the coarse PM, metal concentrations are highest in the afternoon and decrease during the evening time. Coarse PM concentrations are lowest at night and early morning periods. By contrast, the metal concentrations for fine PM are high during late afternoon and evening period (4 to 8 PM hours) and drop at night. The fine PM concentrations are high again during morning (6 to 10 AM) and subside during afternoon (10 to 4 PM hours). These observations can be explained by examining the wind speed at Riverside during different time periods of the day, which is plotted in Figure 35. The average wind speed is low during early morning hours and rises as the day progresses to reach a maximum value in the afternoon around 3 pm. The wind speed decreases again later in the evening. Coarse PM that is primarily produced by wind reuspension is higher during the time at which wind speed reaches a maximum. The peak in fine PM concentrations during evening period (4 to 8 PM) could be attributed to the urban aerosol plume originally emitted by vehicular sources around downtown Los Angeles, coupled with the decrease in mixing height that begins in the early evening. Considering that downtown Los Angeles is about 50 to 60 miles east of Riverside, fine aerosols emitted mostly during the early morning traffic hours should arrive in Riverside by 4 to 6 pm, which is the period during which the highest concentrations are observed. In the absence of any immediate sources in the vicinity, fine PM concentrations drop at night and early morning periods in Riverside. The fine PM bound metal concentrations reach a minimum during afternoon (10 AM to 4 PM), because of the increase in mixing depth as well as wind speed during that period both of which tend to disperse the fine PM.

## **10. Interactions with Other Agencies and Individual Investigators.**

The data that have already been-(or will be) generated by our Supersite have already become a valuable resource for a variety of agencies and individual investigators. These interactions and collaborative activities are summarized in the following paragraphs.

The California Air Resources Board (CARB) and the South Coast AQMD will contribute about \$200,000 for a three year period, starting in the fall of 2001, for a field monitoring study in which the Scanning Mobility Particle Sizer (SMPS 3936, TSI Inc.) and low temperature TEOM (TEO 1400A, R&P Inc.) will be deployed in three of the Children's Health Study (CHS) at a time for a period of 3 years. Of that amount, about \$120,000 will be covered by the ADMQ through funds offered by EPA's region IX to assist the LA Supersite program. CARB will cover the remaining \$80,000 and has already available instrumentation of about \$350,000 to support this study. The proposed activities will make it possible for the first time in the air pollution history to generate unique data on the properties of ultrafine particles in near-continuous time intervals and in 3 several locations of the LA Basin at a time. The deployment of these new air-monitoring technologies will improve what is known about the nature of ultrafine, PM<sub>1</sub> and PM<sub>10</sub> particulate matter in the USC Children's Health Study (CHS) communities and thus provide unique exposure data that will be readily linkable to ongoing health studies and of direct use in assessing the association between respiratory health and ambient particle exposure. Furthermore, the deployment of SMPS would provide investigators of the Southern California Particle Center with unique data on the size distributions of fine and ultrafine PM in "source" and "receptor" sites of the LA Basin, which will be essential in developing and validating predictive models on PM formation and transport mechanisms in the Basin. This will be accomplished by monitoring in real-life, PM formation and growth as the urban PM plume moves along predominant air trajectories, such as the "nitrate" or the "vehicle" trajectory.

Finally, two projects (supported by the EPA STAR program and the National Institute of Health, respectively) will commence this September, of which will make use of the LA

Supersite data. The objective of the EPA STAR proposal, led by Dr. Jack Harkema (Michigan State University) is to conduct atmospheric and toxicologic research designed to understand the adverse effects of airborne particulate matter (PM) of various size fractions (coarse, fine, and ultrafine particles) on airways with allergic airway disease. An integrated investigative team of environmental and biomedical scientists from Michigan State University (MSU) and the Southern California Particle Center and Supersite (SCPCS) will conduct atmospheric and toxicologic research at three Supersite sites in the Los Angeles Basin, each of which have distinct air-pollution profiles. Physico-chemical analysis of particles and co-pollutants in that study will be provided by the LA Supersite. The NIH proposal, led by Dr. Ralph Delfino (UC Irvine), will make use of the LA Supersite data generated in Boyle Heights (source site) and Riverside/Rubidoux (receptor sites) to investigate the whether personal exposure to particulate air pollution interact with or explain the effects of NO<sub>2</sub> on asthma morbidity.

## **10. Progress on Site identification and Deployment of the PIU**

A key feature of our Supersite activities was the ability to conduct state-of-the-art measurements of the physicochemical characteristic of PM in different locations of the Los Angeles Basin (LAB). We have proposed a 2.5-year repeating cycle of measurements at five locations. Each location will be sampled during a period of intense photochemistry (defined approximately as May – October) and low photochemical activity (defined as the period between November – April). In early March 2001, we identified and secured our last site in Claremont. The site is property of the Southern California Water Company and it is ideally located in the foothills of the San Bernardino Mountains, right along the “vehicle-oriented” trajectory. The site has ample power readily available to support our PIU as well as our PM center activities. The PIU is scheduled to be transported to Claremont during the 2<sup>nd</sup> week of September, 2001.

Sampling in our Rancho Los Amigos has been completed. Sampling in Riverside started during the 3<sup>rd</sup> week of February 2001. The PIU remained at Riverside through mid June and was

relocated to Rubidoux between mid June through September 13, 2001. Starting September 2001 we will move to Claremont/Upland, where we will spend the next 4-5 months. Finally, in the winter of 2002 we will move to USC campus (an upwind freeway site). It should be noted that this is a tentative plan and it may be subject to changes, depending on the needs of our PM Center investigators who will be using these data.

Consistent with our original proposal, we have been conducting the “freeway study” and the characterization of PM and gaseous co-pollutants as a function of distance from a freeway. Sampling (concurrently with animal exposures) at USC started during through last week of April 2001. The main campus of USC is our upwind site, as it is located more than 1 mile to the west or south of freeways 110 and 10, respectively. Over the next few months, measurements will be taken in our site in Boyle Heights, which is downwind of Freeway 5 and is located 15-20 meters away from the freeway. Additional PM and copollutant measurements will be taken in discrete distances and perpendicularly to Freeway 5, in conjunction with inhalation exposure studies to concentrated PM from the freeway, utilizing the USC particle concentrators.

## 11. References

Luhrman, F.W., Wexler, A.S., Pandis, S.N., Musarra, S., Kumar, N., and Seinfeld, J.H. (1997). Modeling urban and regional aerosols-II. Application to California's South Coast Basin. *Atmospheric Environ* 31:2695-2715

Sioutas, C., Kim, S., and Chang, M. "Development and evaluation of a prototype ultrafine particle concentrator." *Journal of Aerosol Science*, 30 (8):1001-1012, 1999.

Misra, C., Geller, M., Sioutas, C and Solomon P. "Development and evaluation of a continuous coarse particle monitor". Manuscript submitted for publication in *Journal of Air and Waste Management Association*, January 2001.

Cass, G. "Formation and control of nitrogen-containing air pollutants". Final report prepared for California Air Resources Board, EQL report 24, 1987.

Figure 1. Chemical species in the 5 PM10 sub modes, Downey and Riverside

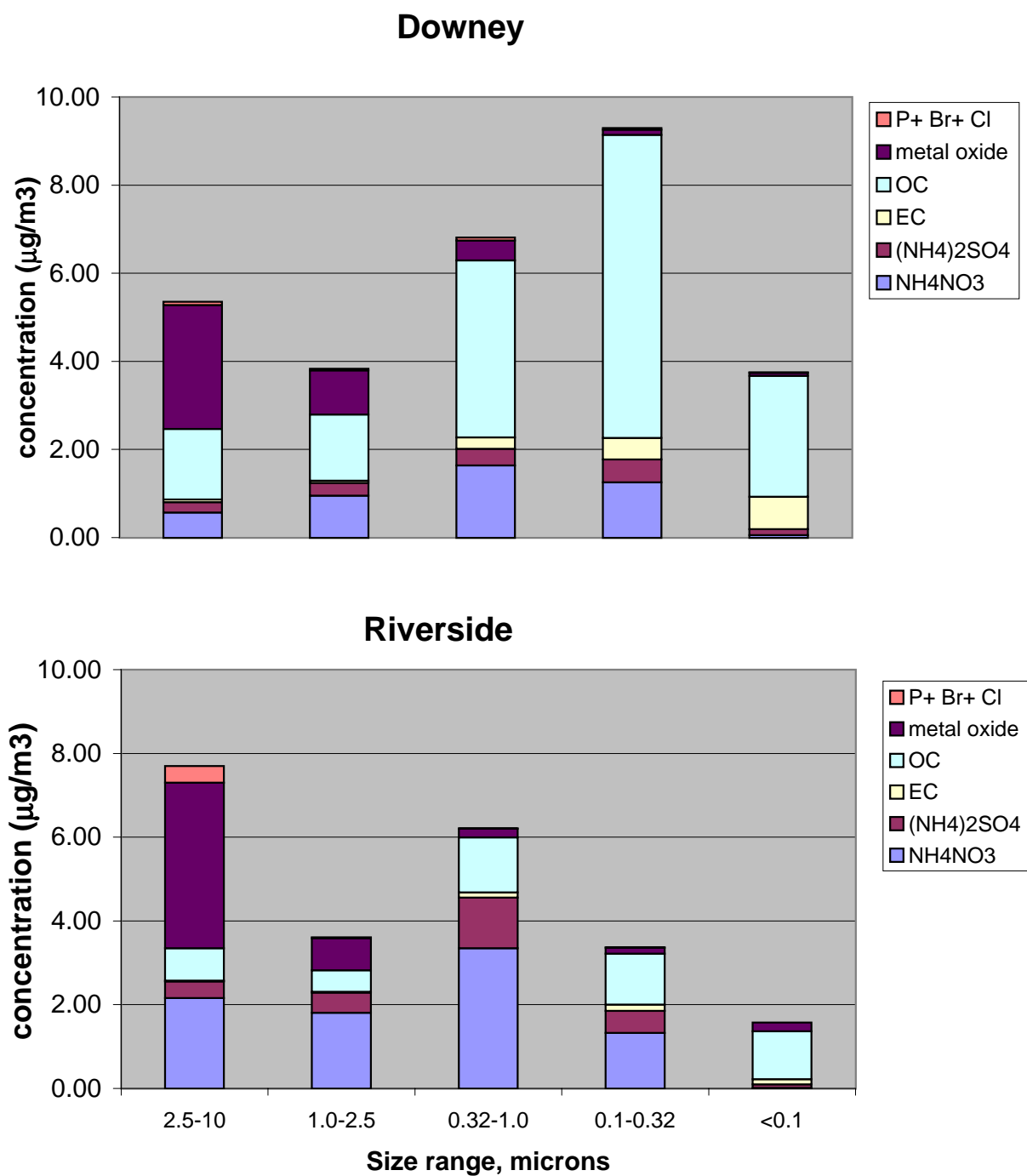




Figure 2. PM10 Fraction distribution of Single Chemical species

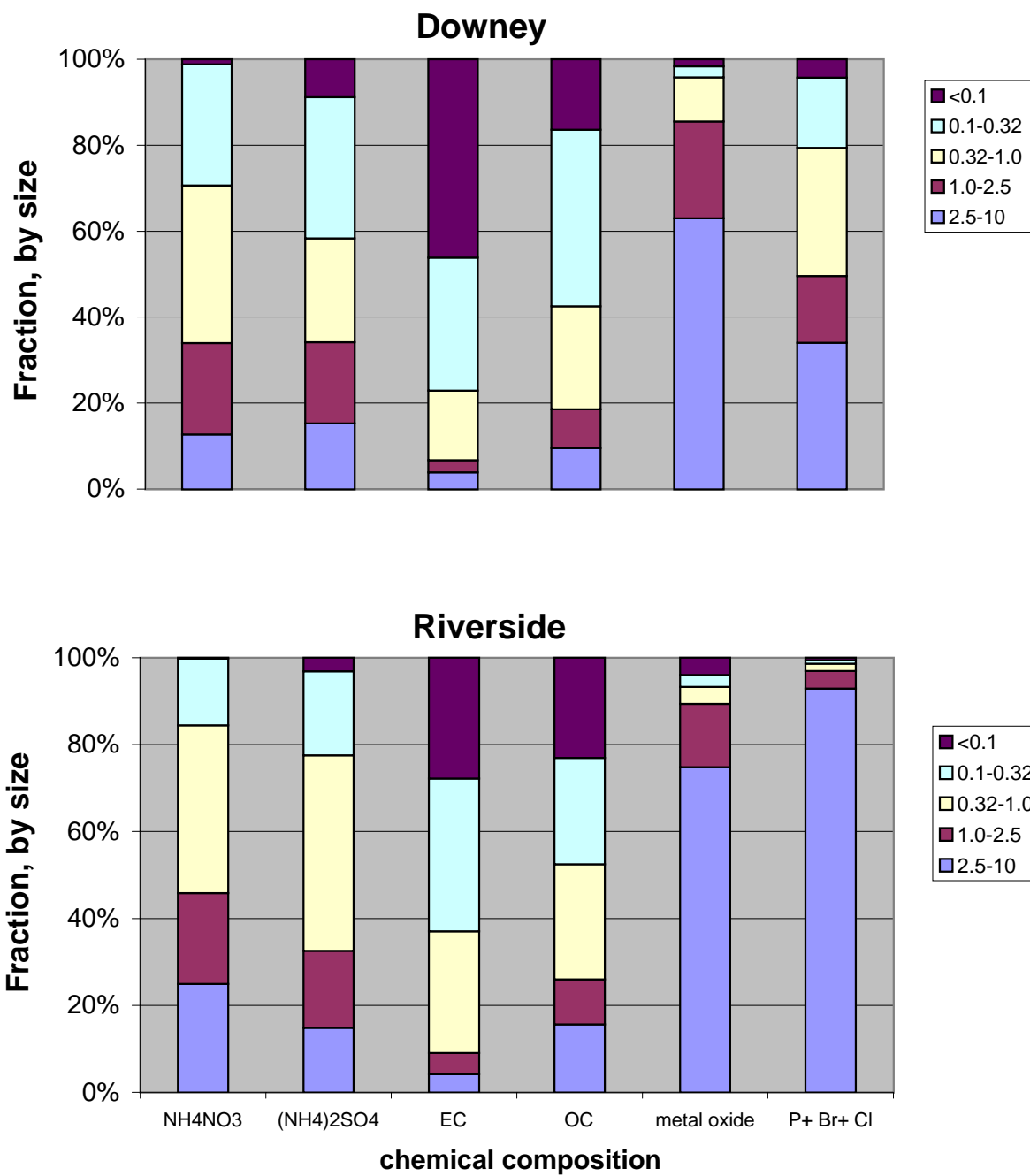
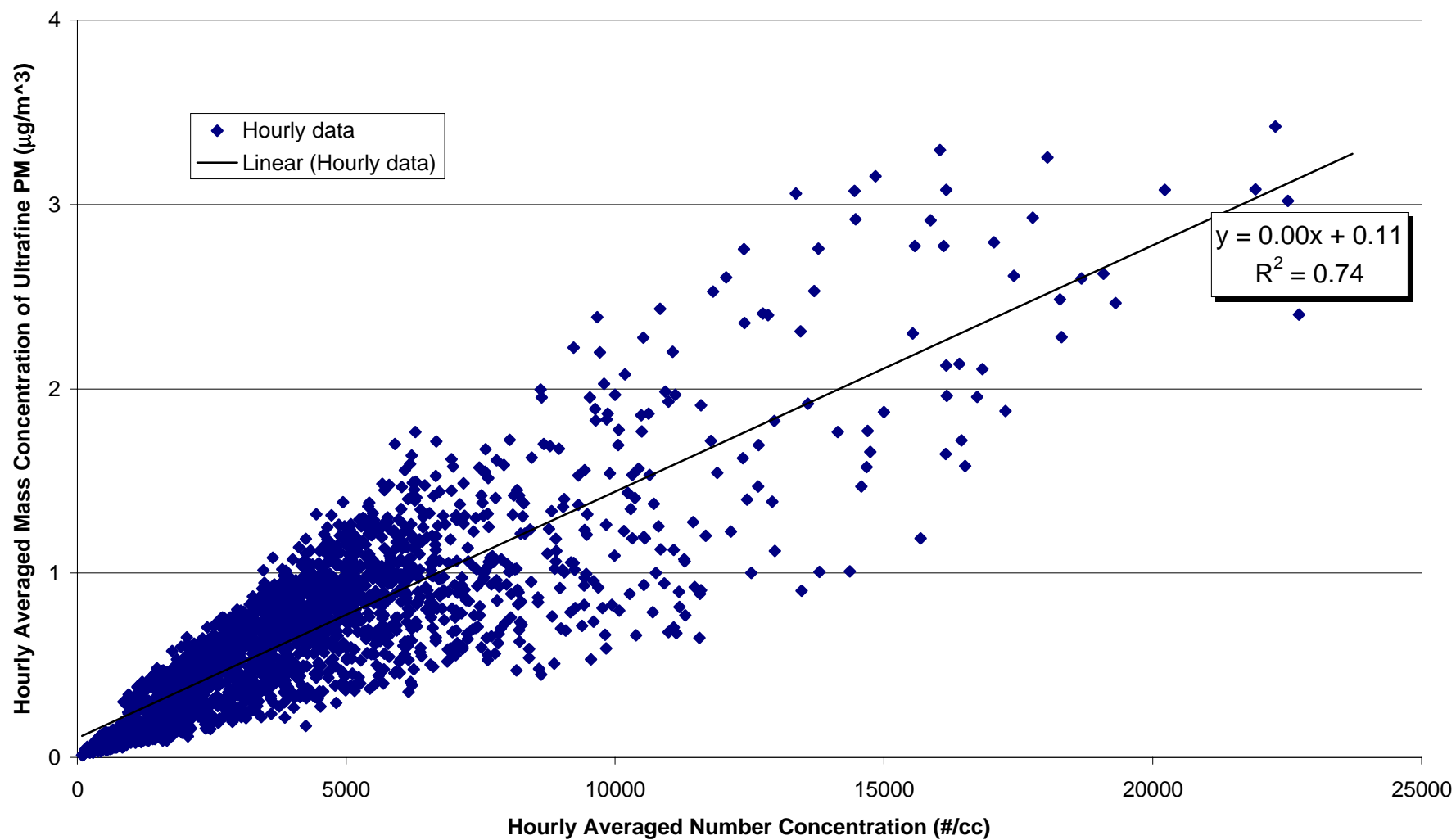
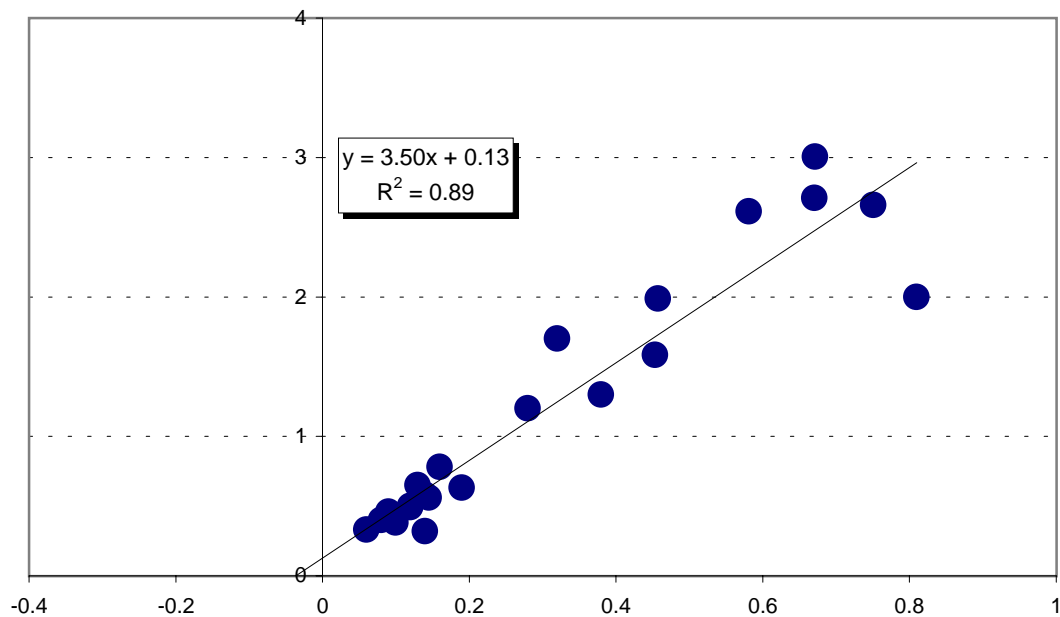


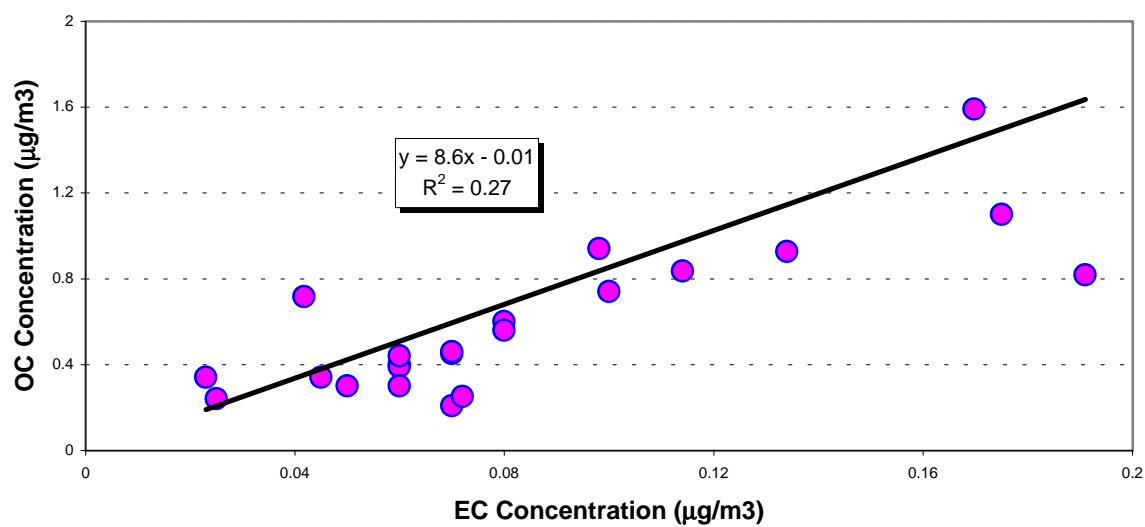
Figure 3. Hourly averaged number and mass concentrations of ultrafine PM : October,2000 - June, 2001



**Figure 4 (a) 24-hour OC vs EC concentrations of Ultrafine PM in Downey October 2000 - February 2001**



**Figure 4 (b) 24 hour Average OC vs EC Concentration of Ultrafine PM in Riverside. February - May 2001**



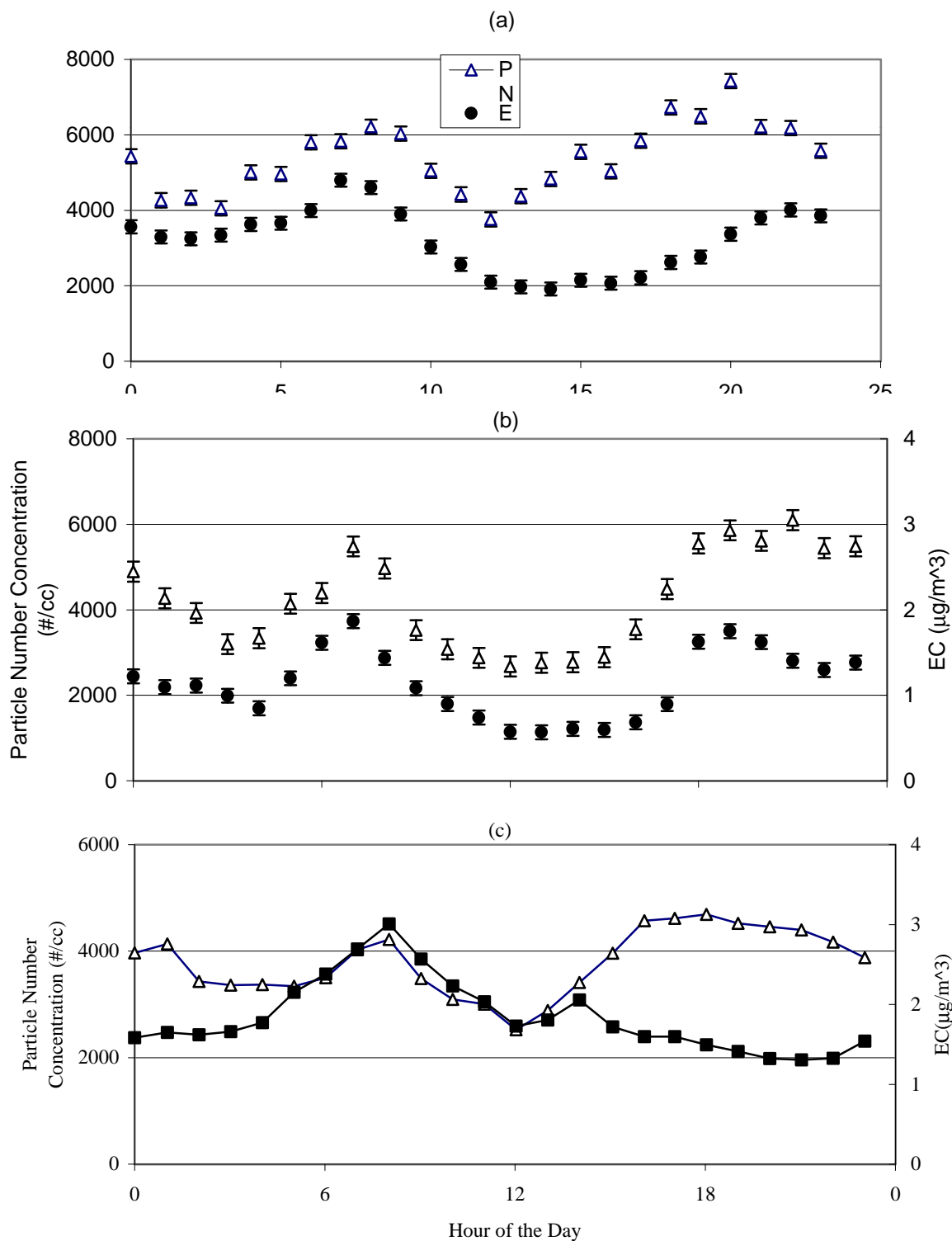


Figure 5. Diurnal pattern of particle number and elemental carbon concentrations averaged over time period (a) at Downey from October, 2000 to January 2001, (b) at Riverside in February 2001, and (c) at Riverside in May 2001.

Figure 6 (a) Monthly averaged geometric mean diameters vs hour of the day  
Downey, CA

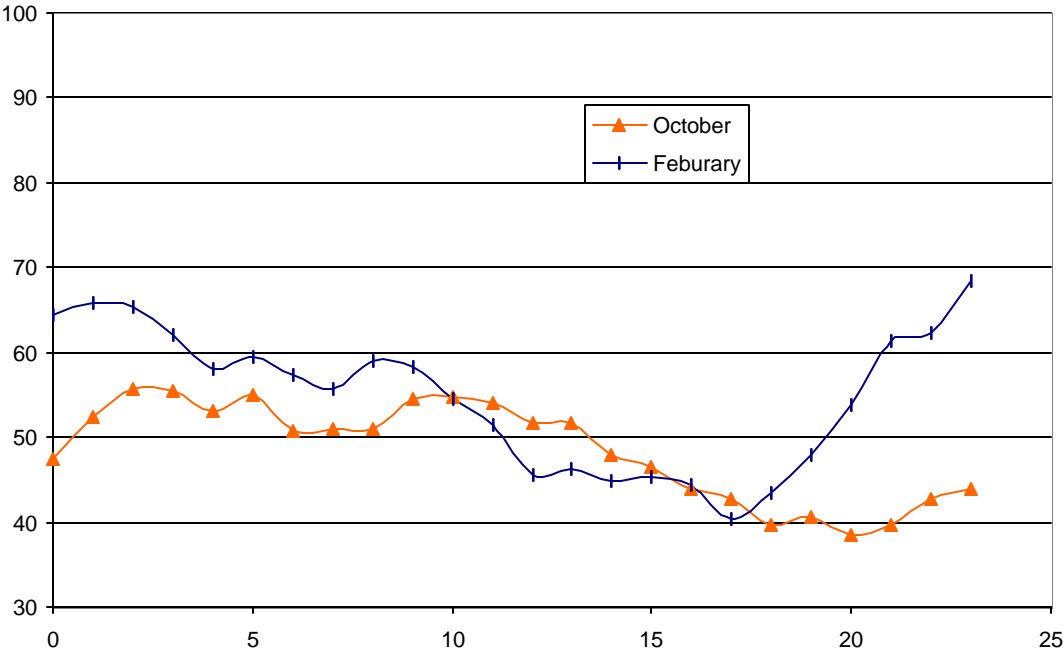
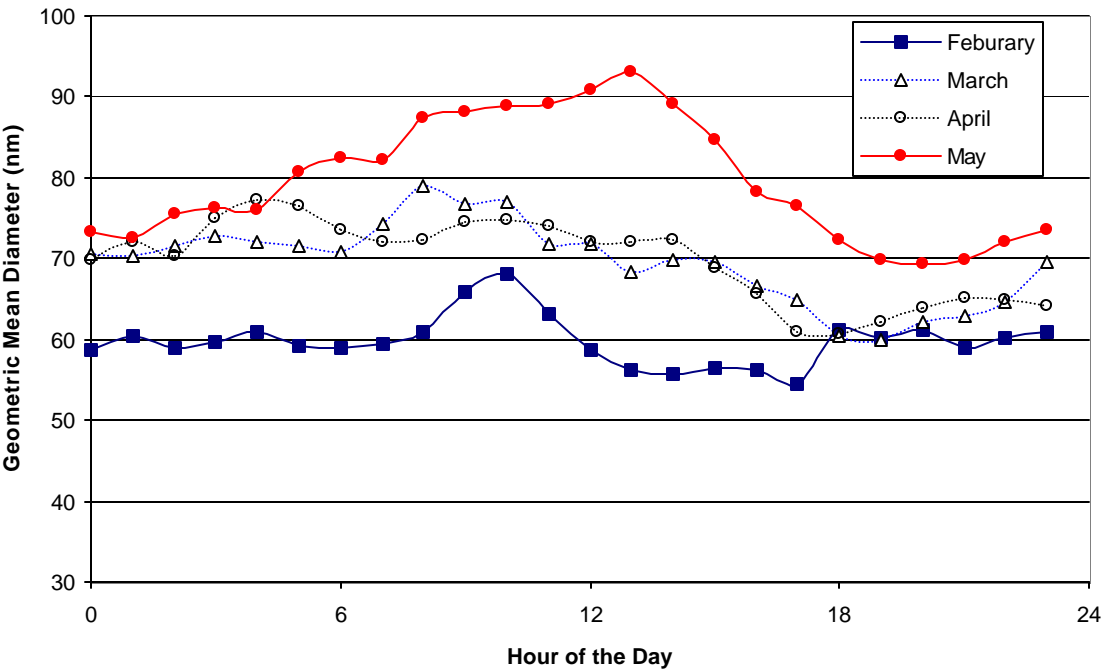


Figure 6 (b) Monthly avraged geometric mean diameters in 24 hours  
Riverside, CA, 2001



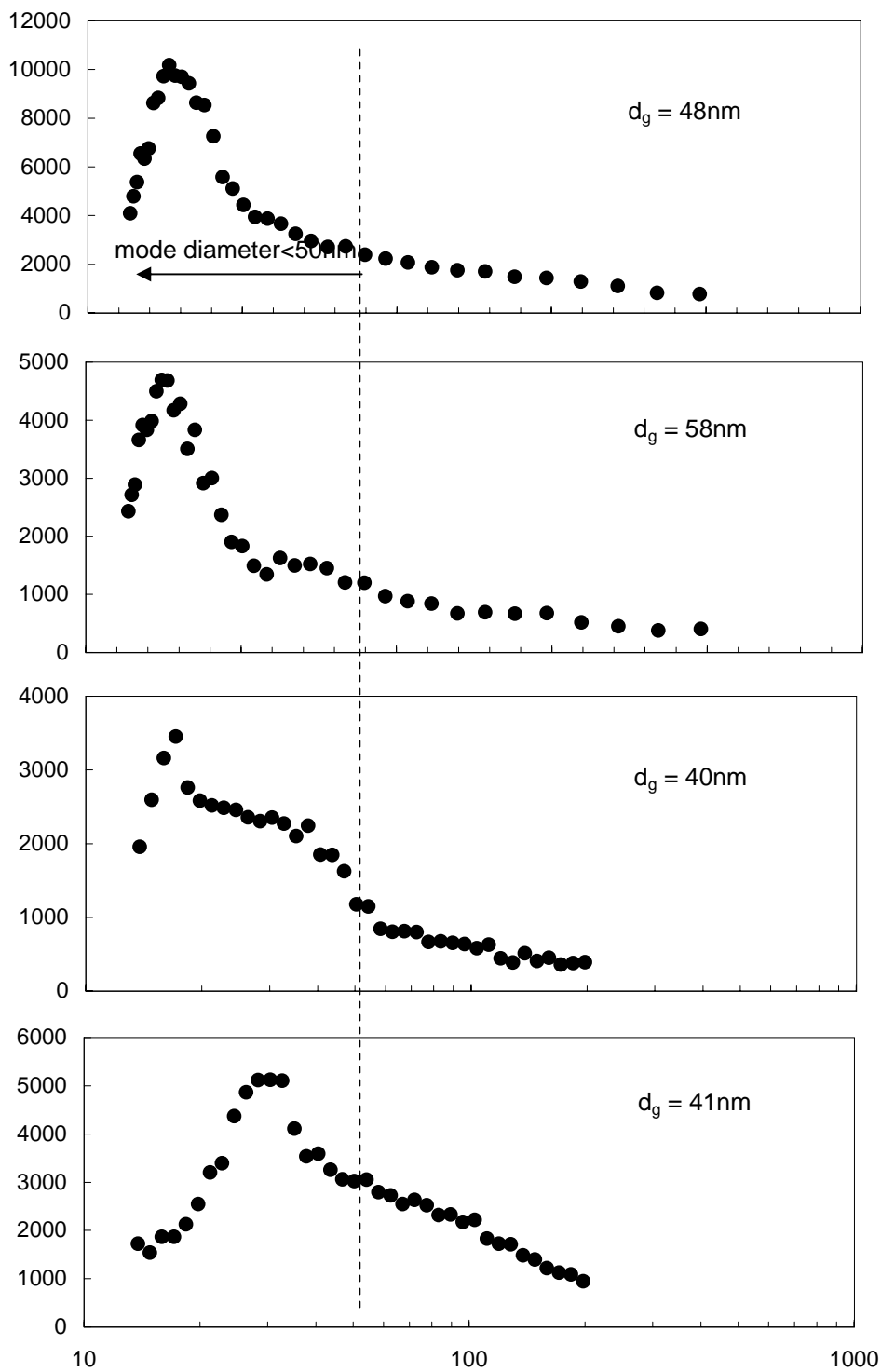


Figure 7. Size distributions of ultrafine particles at Downey, 10/10/2000

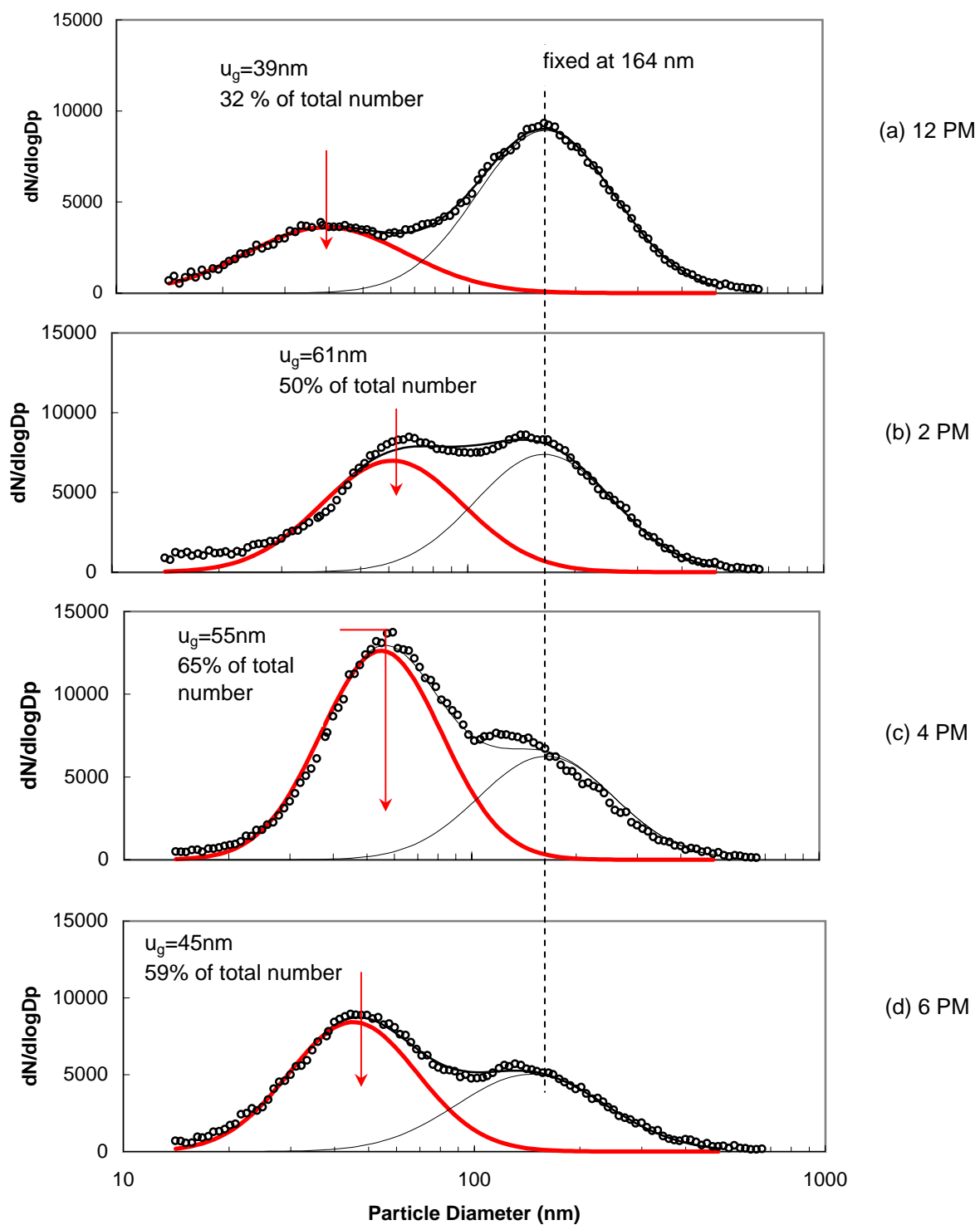
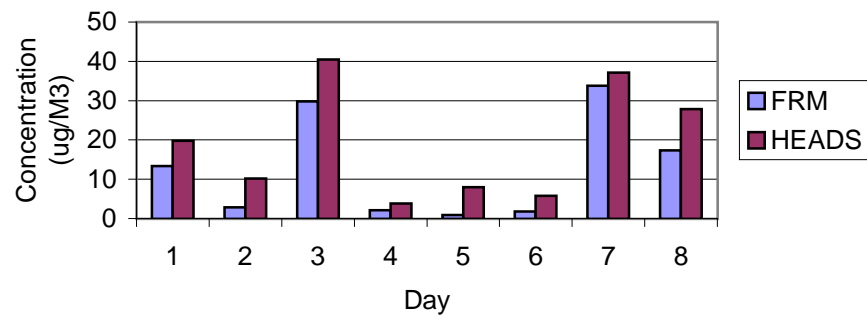


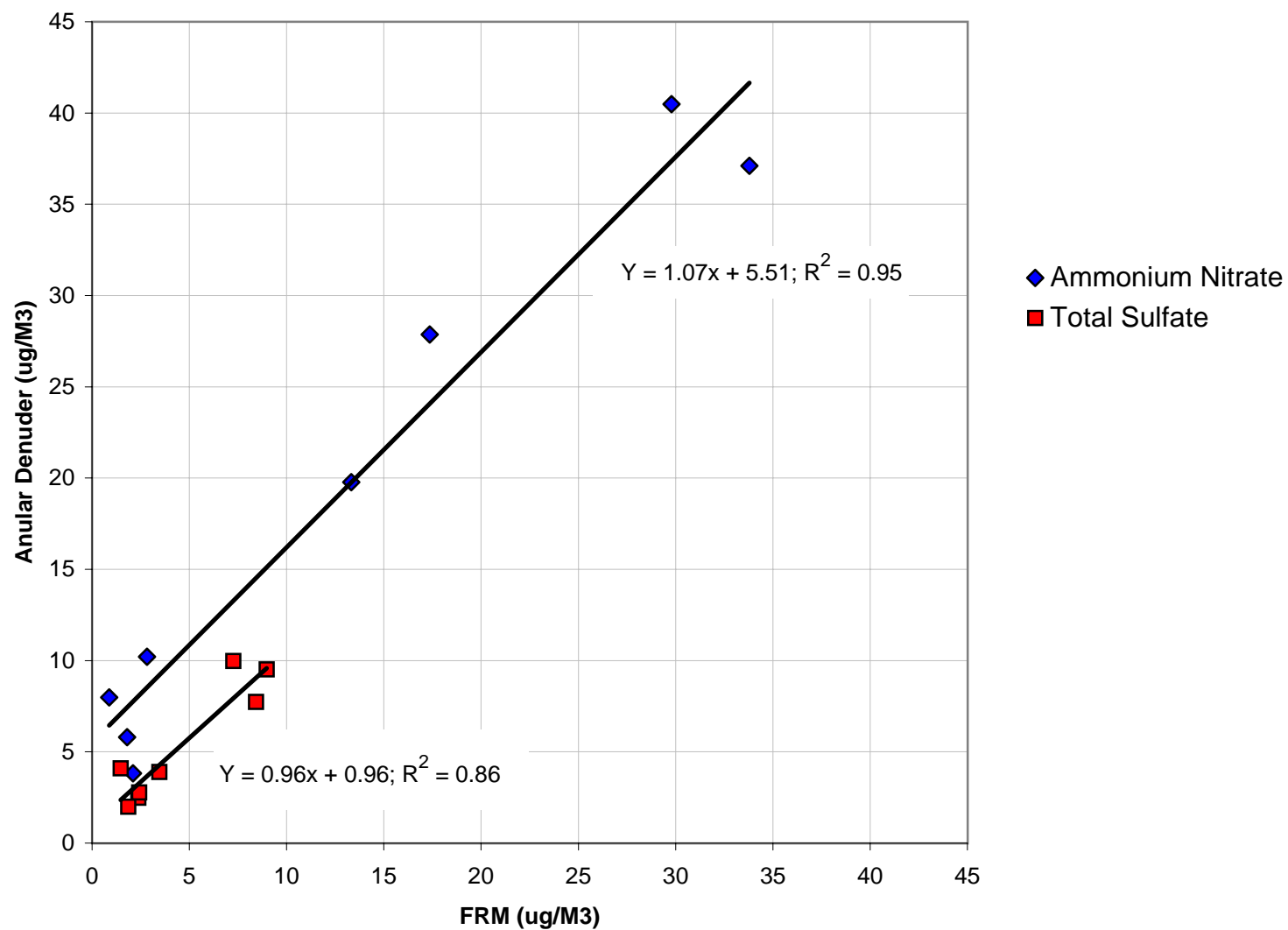
Figure 8. Simulated sub-modes of particles in the afternoon: Riverside, 5/16/2001

Figure 9. Every 3rd day measurements of PM 2.5 Ammonium Nitrate at Riverside (measured by HEADS denuder and Partisol FRM)





**Figure 10. PM-2.5 Ammonium Nitrate & Total Sulfate, Measured by FRM & Annular Denuder, Riverside**



**Figure 11: PM-10 Inlet Collection Efficiency Curve**

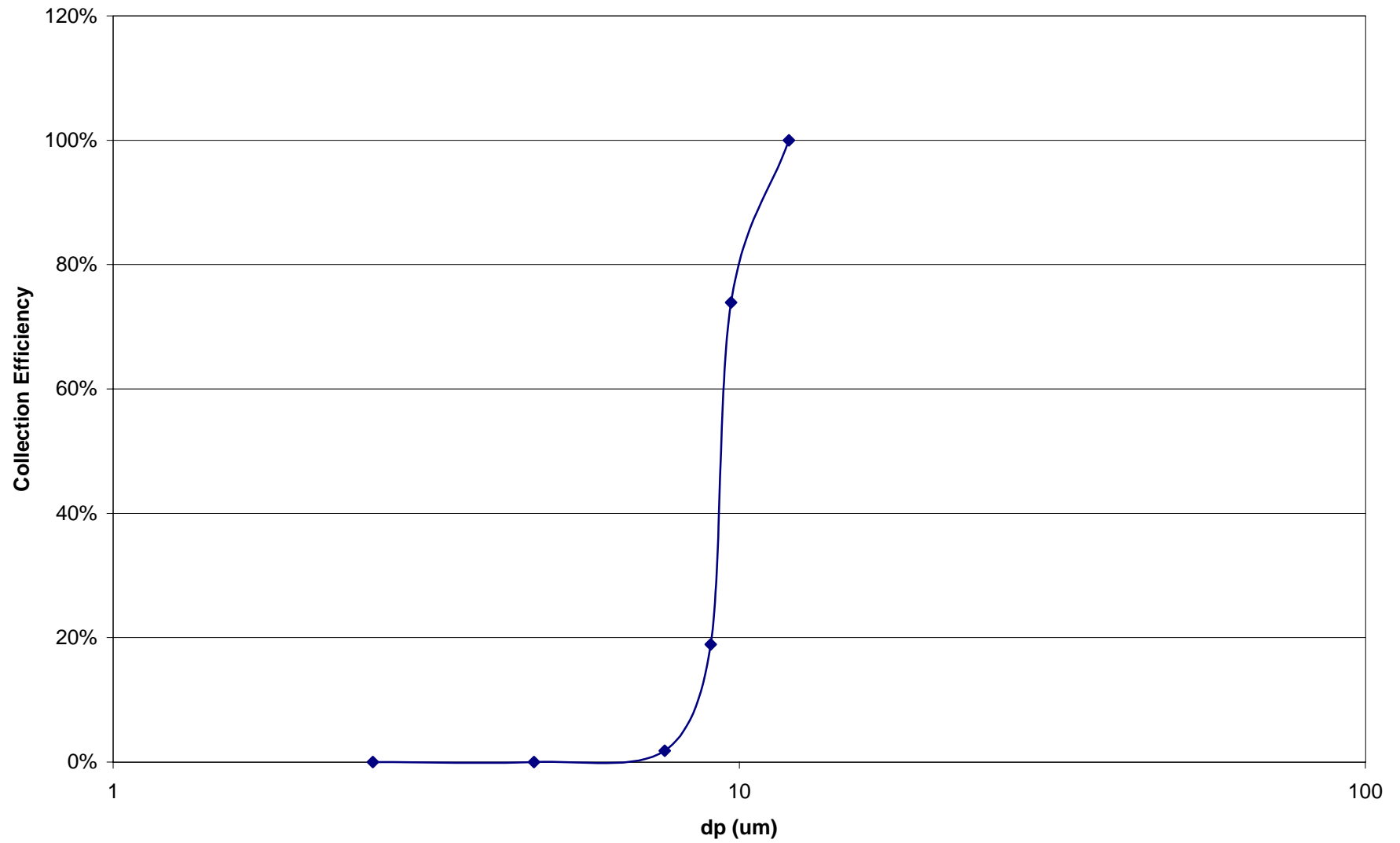
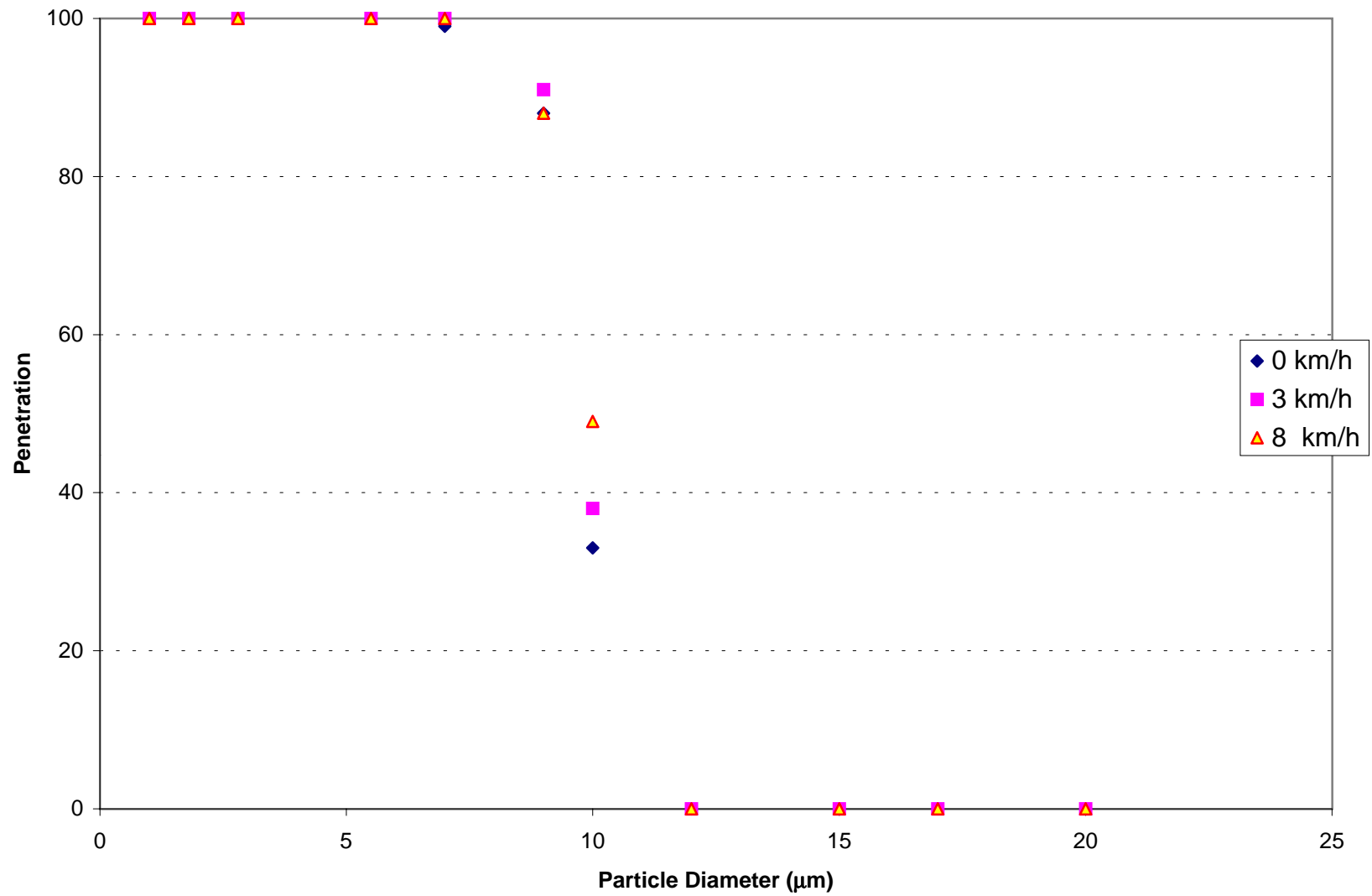


Figure 12: Evaluation of the 50 LPM PM10 FRM Inlet at 3 wind Speeds



**Figure 13: Coarse PM Concentrations Determined by the Coarse Continuous Monitor with the 50 LPM PM-10 FRM and the R&P Partisol**

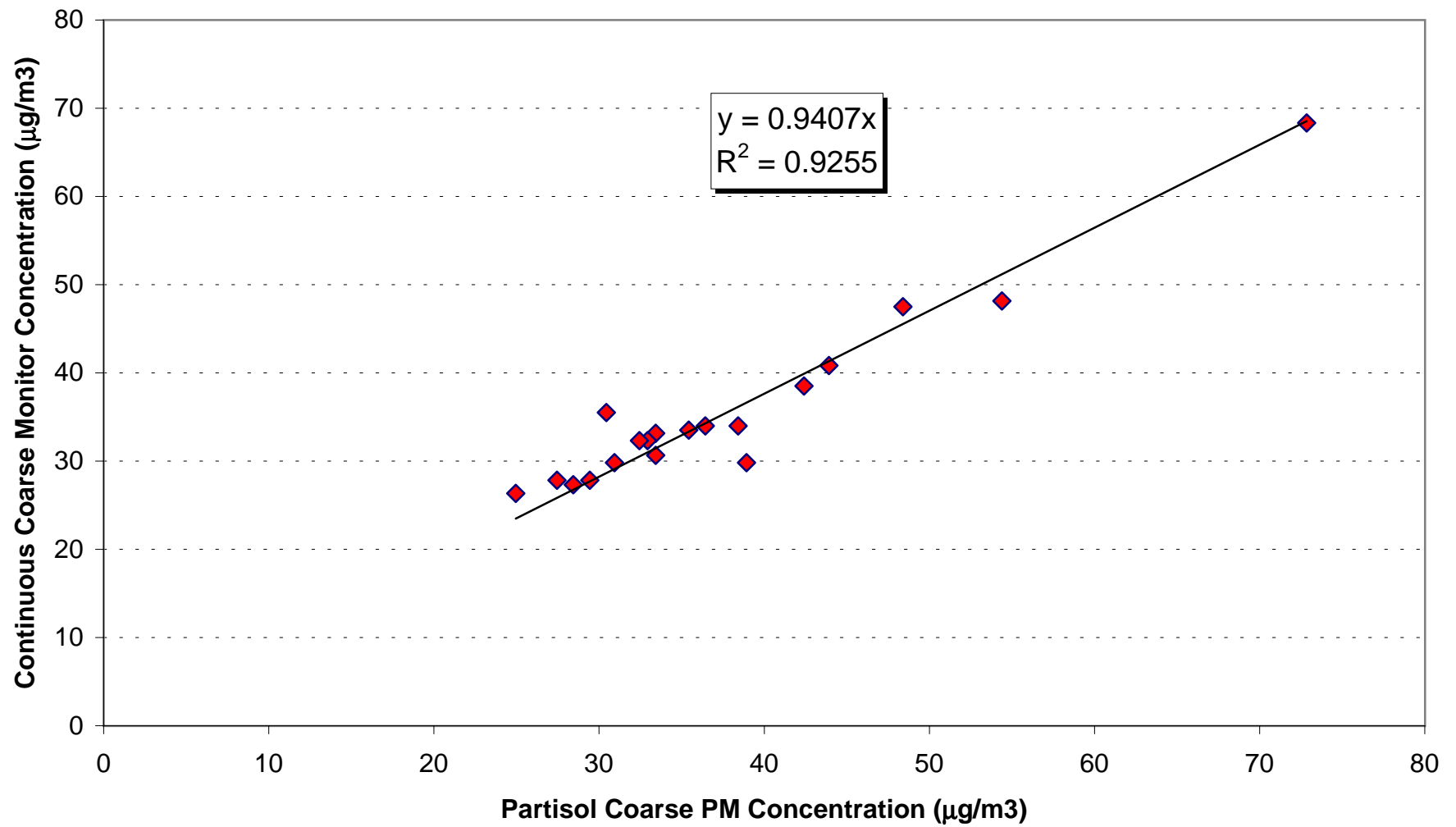


Figure 14. Variation of Daytime Ultrafine Mass Concentration at Downey

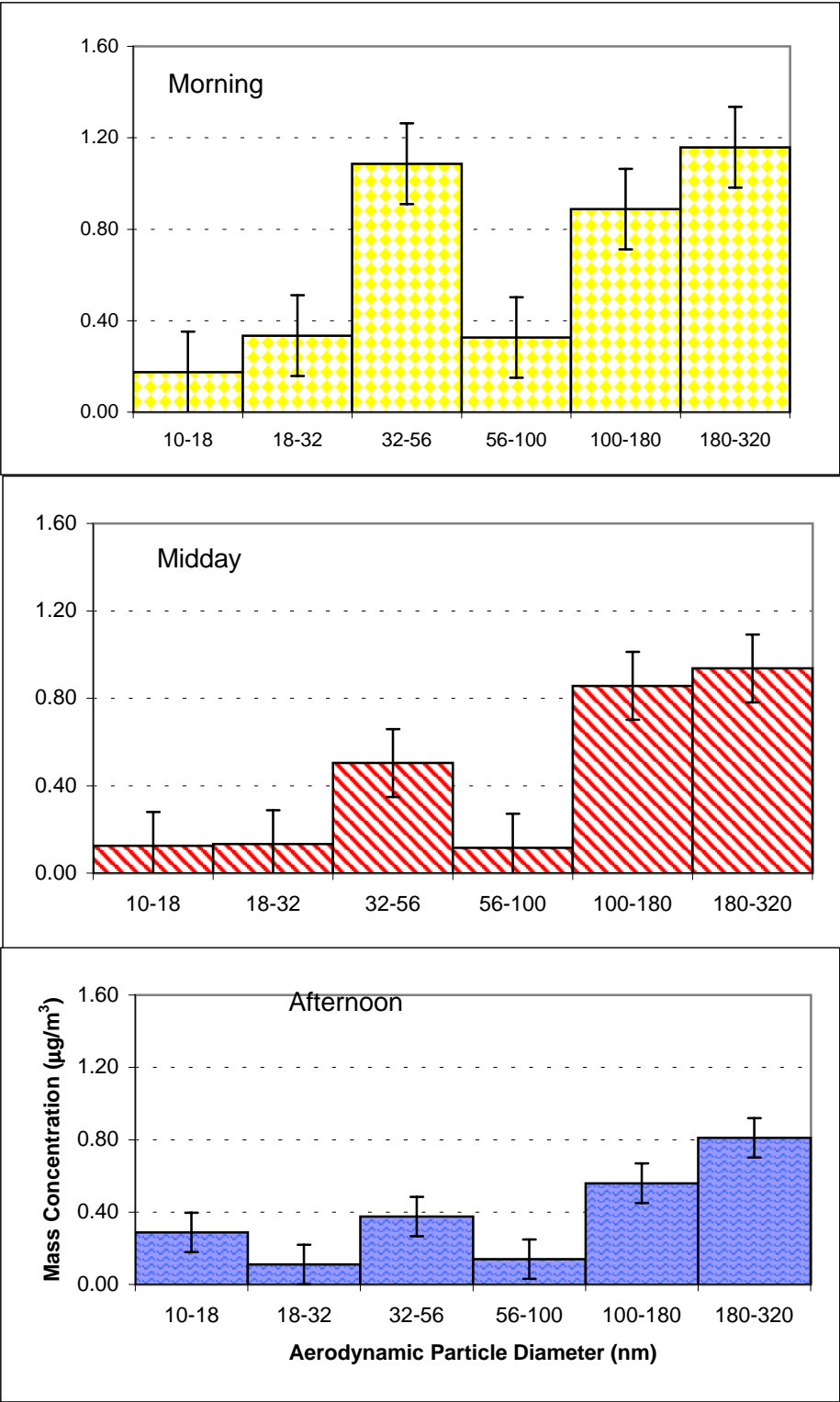


Figure 15. Variation of Daytime Ultrafine Mass Concentration at Riverside

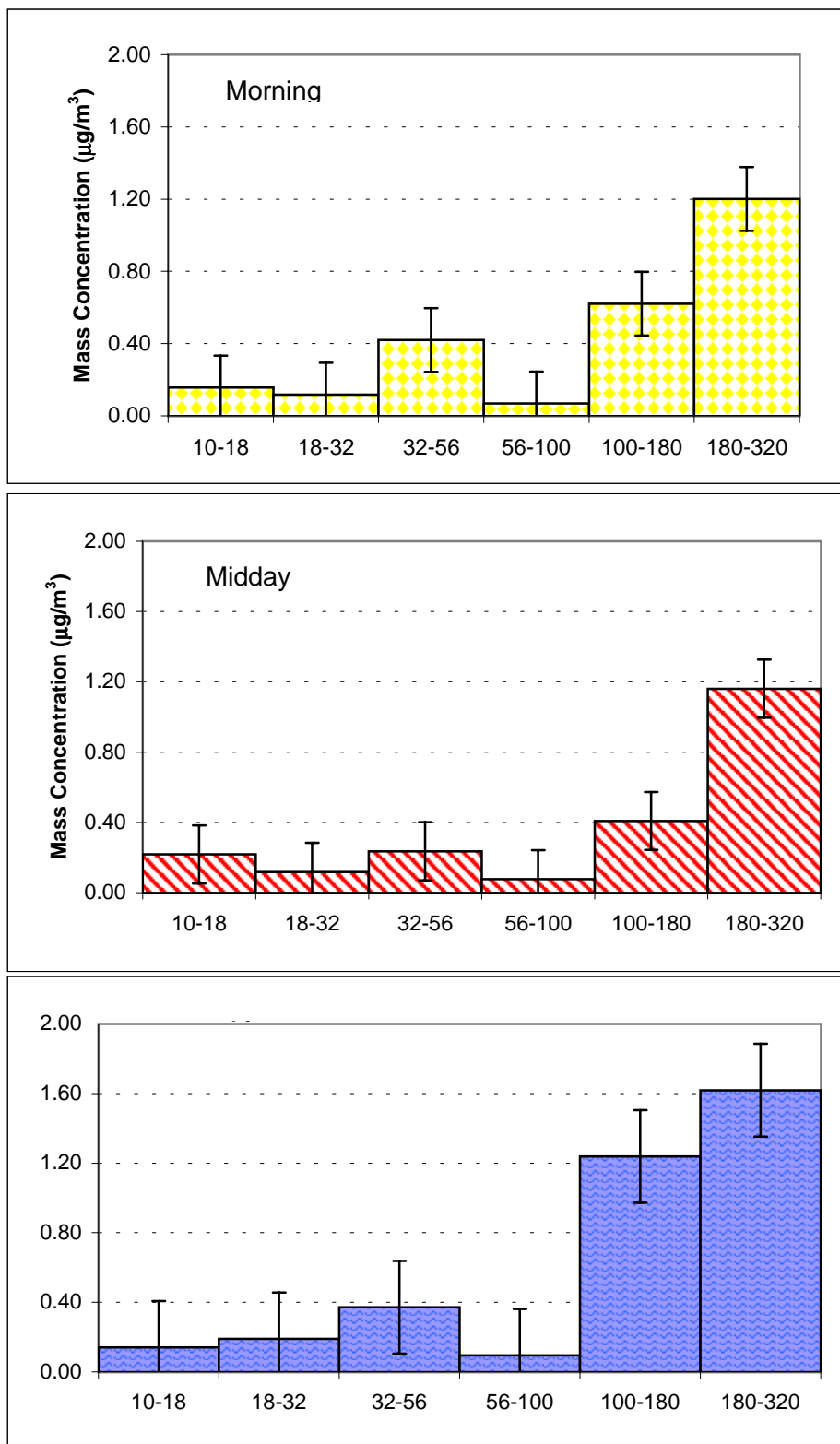


Figure 16. Schematic of the size-segregated ICVS particulate nitrate system.

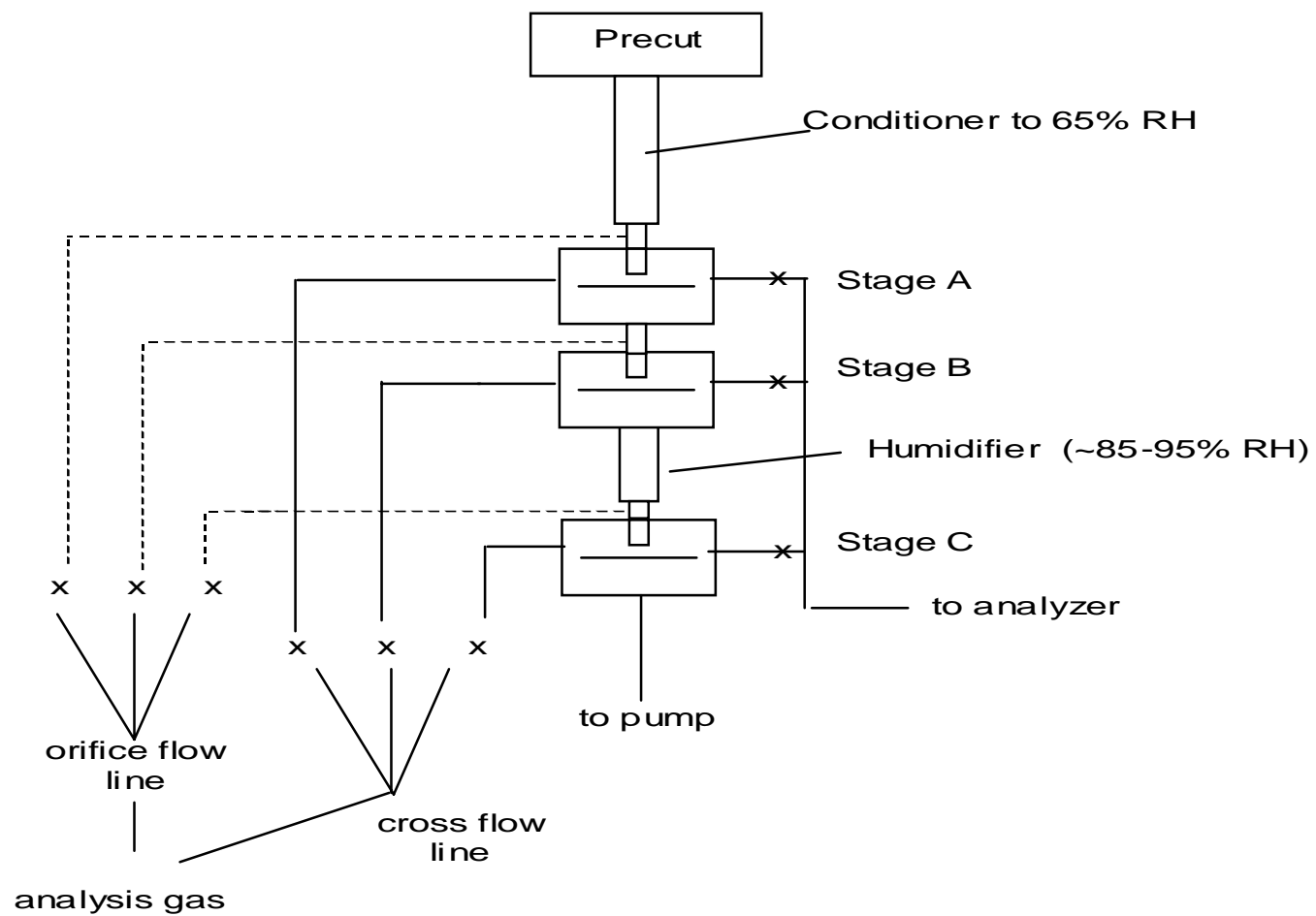
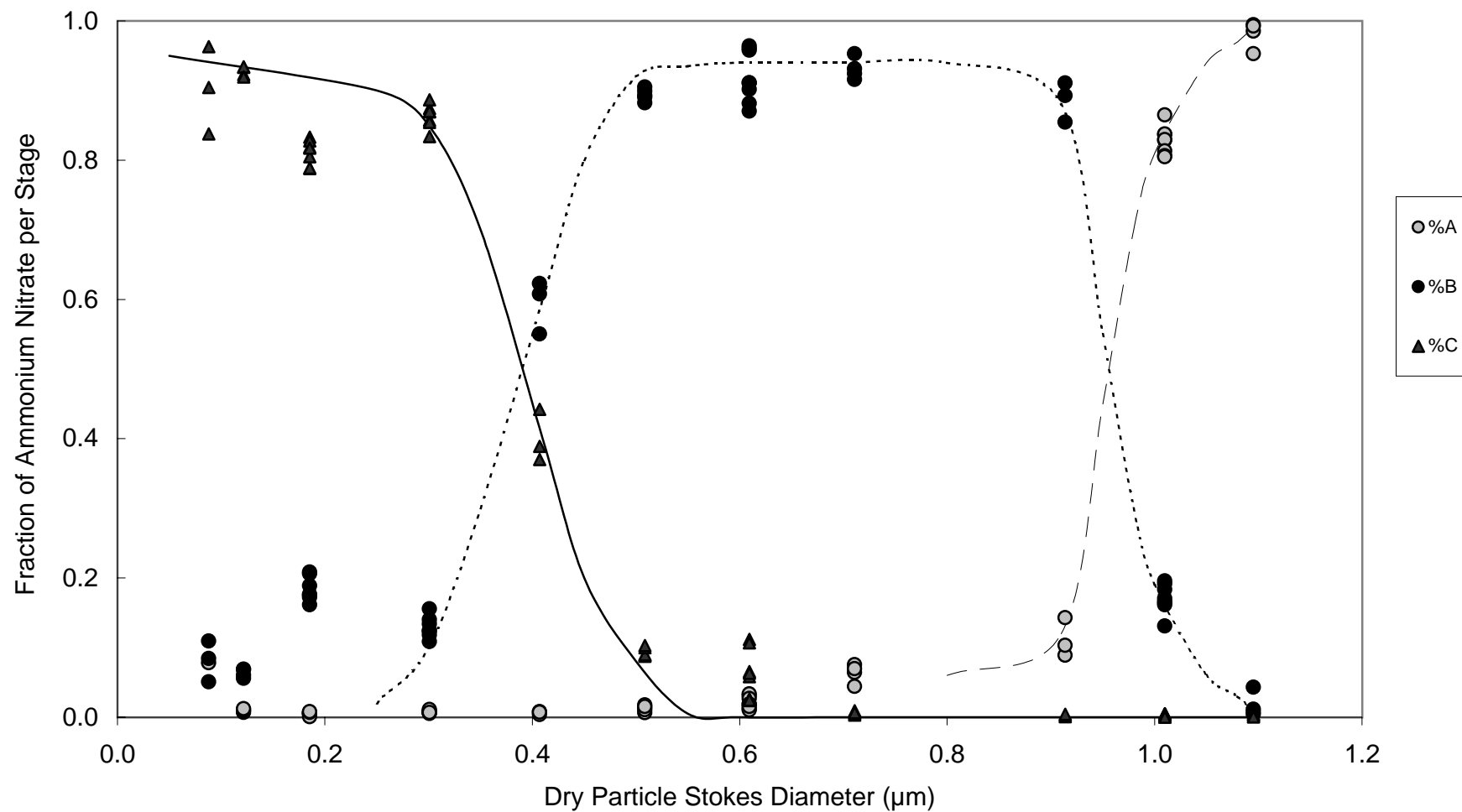
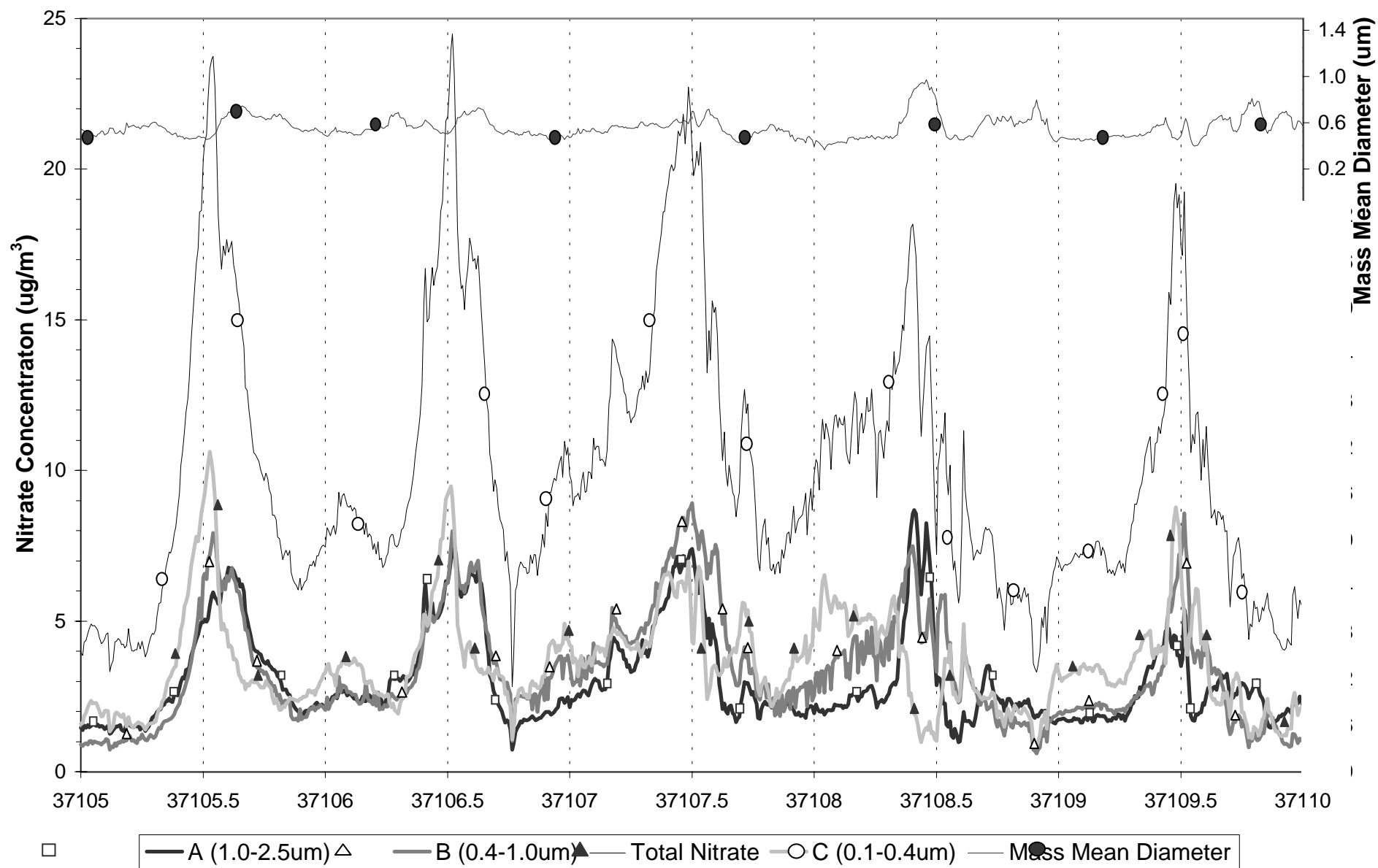


Figure 17. Stage differentiation of size-segregated ICVS. Doublets were avoided or corrected for when possible. Data collected at 0.19  $\mu\text{m}$  include a doublet at 0.30  $\mu\text{m}$  which could not be differentiated.

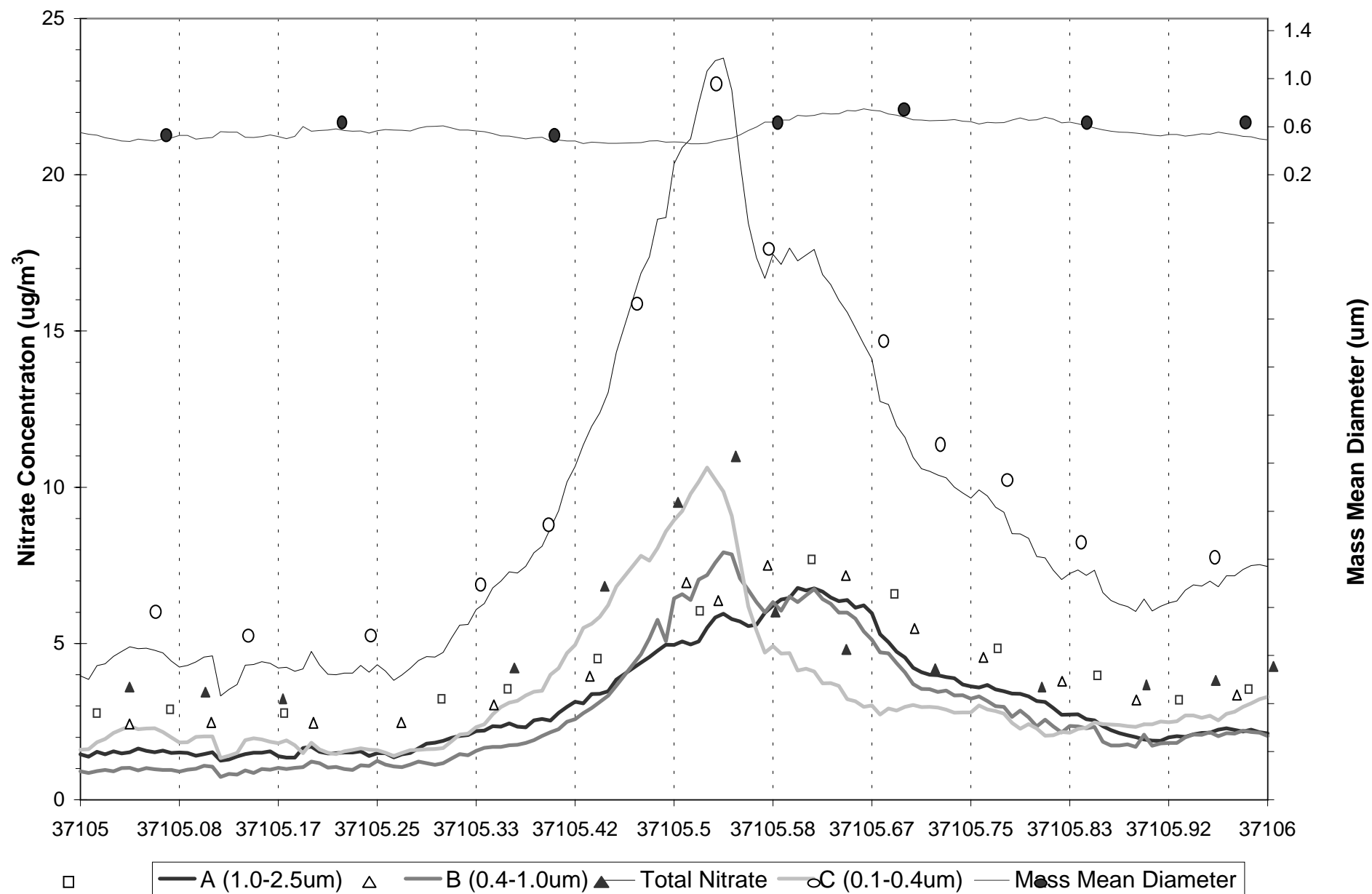




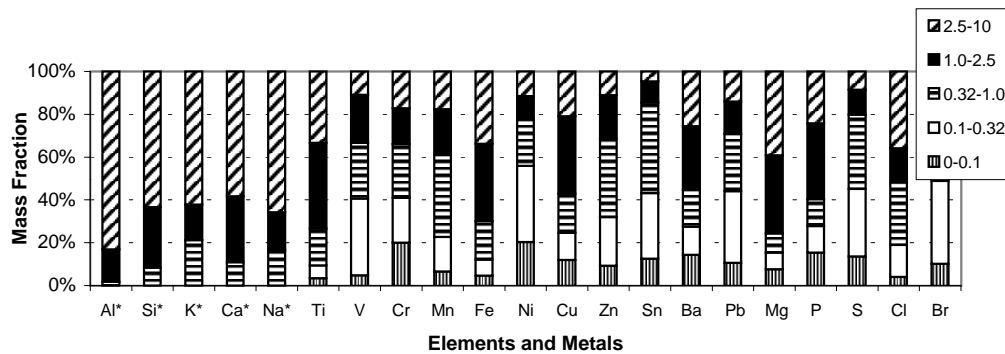
**Figure 18. Size-segregated on-line particulate nitrate measurements, Rubidoux, California. Mass Mean Diameter is a mass weighted average based on the geometric mean of the particle size range for each stage.**



**Figure 19. Size-segregated on-line particulate nitrate measurements, Rubidoux, California. Note the time separation of peaks for Stage A vs. Stages B and C.**

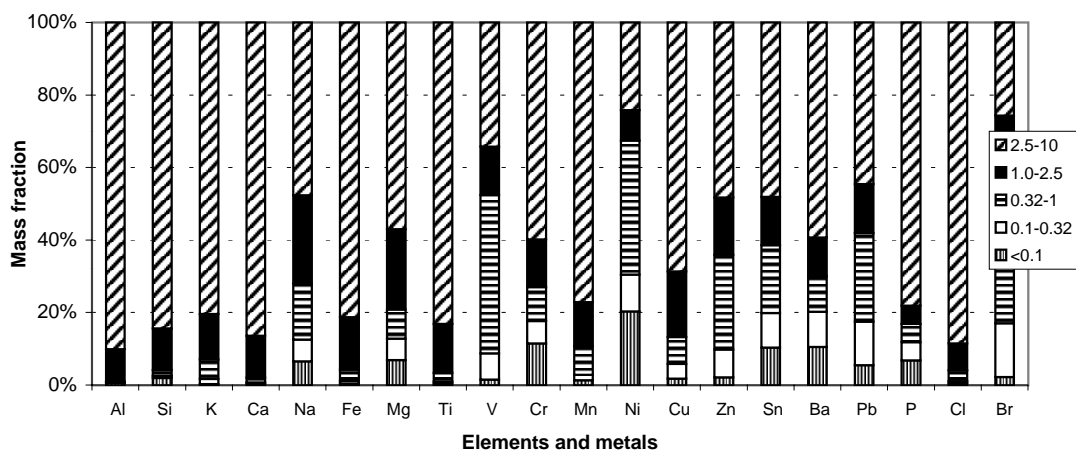


**Fig. 30a: Fractions of metals and elements in 5 particle size ranges in Downey, CA, October 2000- February 2001, N=13 (N=7 for Na and Mg).**

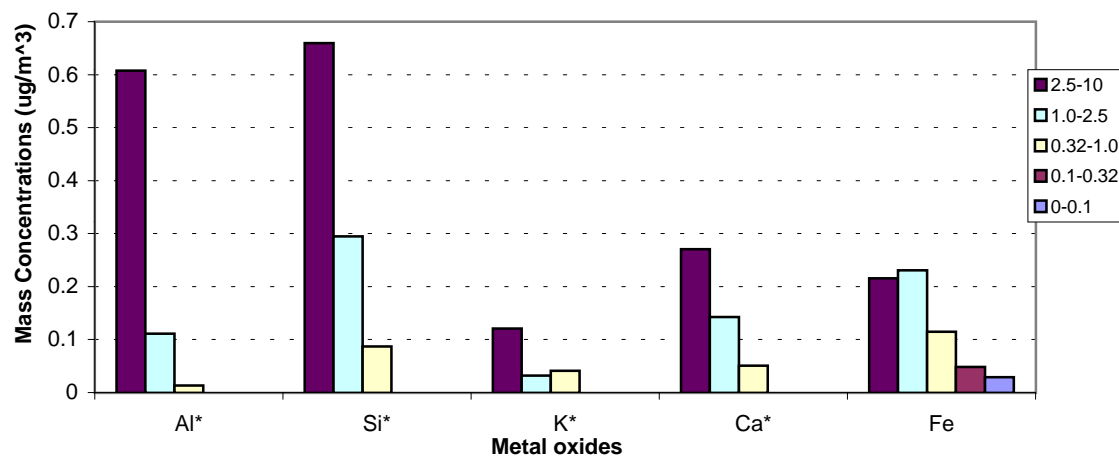


\*Metal oxides collected in 0-0.1 and 0.1-0.32  $\mu\text{m}$  particle size ranges were assumed to be coarse particles (2.5-10 $\mu\text{m}$ ) bouncing and penetrating onto the impactors for 0-0.1 and 0.1-0.32  $\mu\text{m}$  particles. Thus, the fractions in these two particle size ranges were included in the one for the coarse fraction.

**Fig 30b: Fractions of metals and elements in 5 particle size ranges in Riverside, CA, March-June 2001(N=13)**

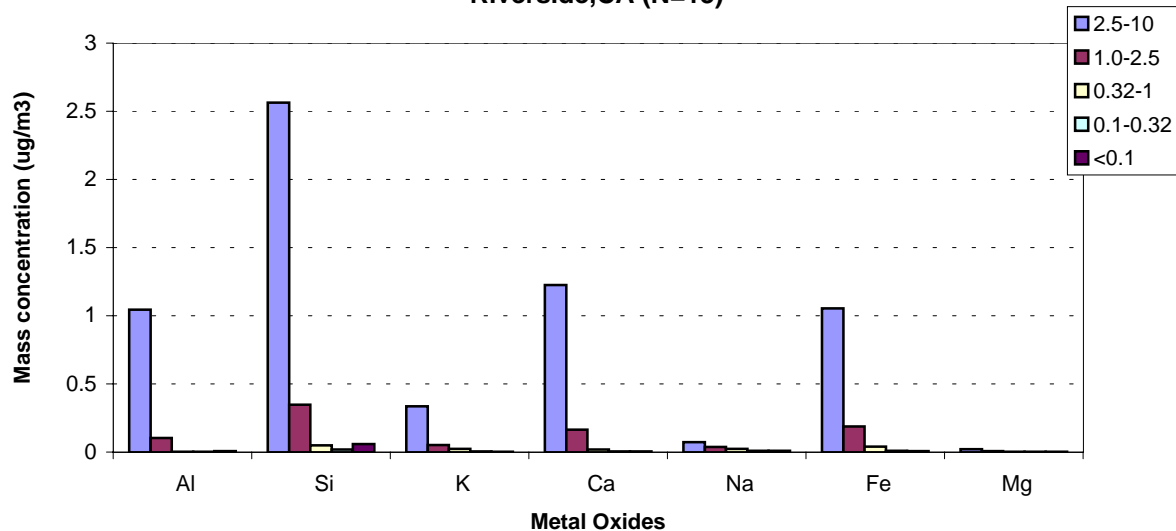


**Fig. 31a: Crustal metal oxide concentrations in 5 particle size ranges in Downey, CA ( N=13).**

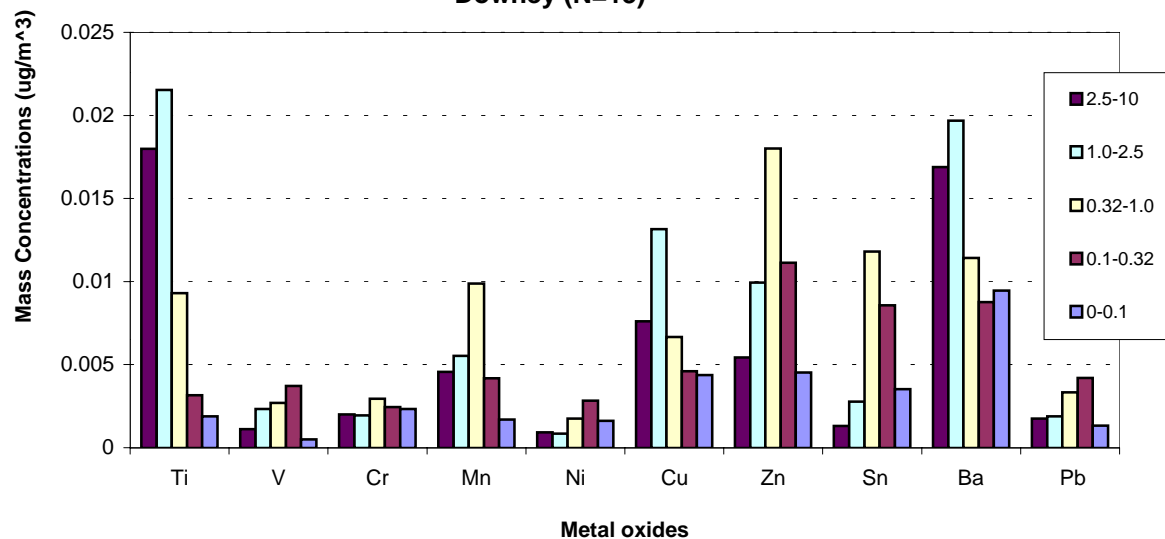


\*Metal oxides collected in 0-0.1 and 0.1-0.32  $\mu\text{m}$  particle size ranges were assumed to be coarse particles (2.5-10 $\mu\text{m}$ ) bouncing and penetrating onto the impactors for 0-0.1 and 0.1-0.32  $\mu\text{m}$  particles. Thus, the fractions in these two particle size ranges were included in the one for the coarse fraction.

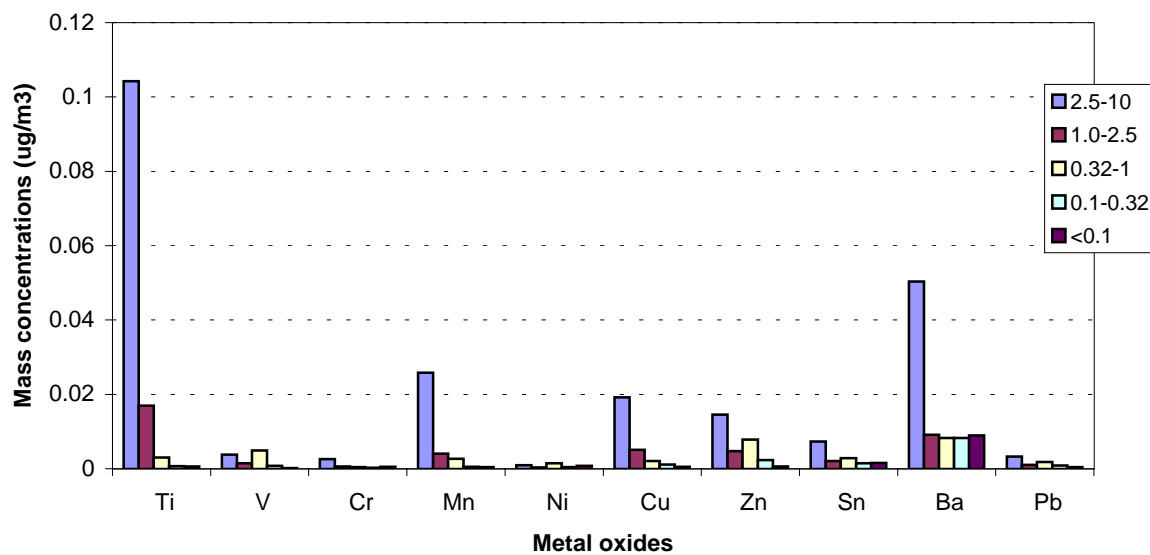
**Fig 31b : Crustal metal oxide concentrations in 5 particle size ranges in Riverside,CA (N=13)**



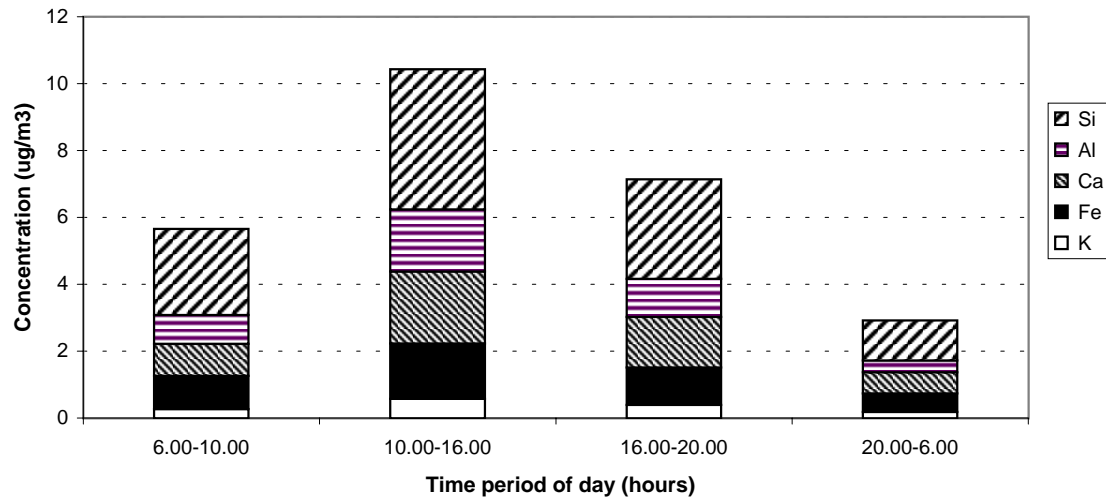
**Fig.32a: Concentration of selected metal oxides in 5 particle size ranges in Downey (N=13)**



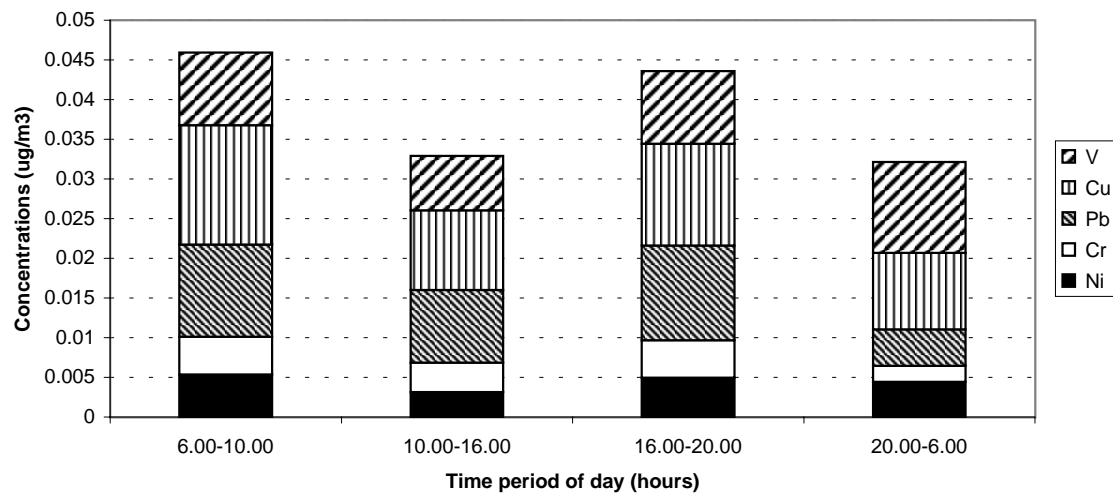
**Fig. 32b: Concentration of selected metal oxides in 5 particle size ranges in Riverside,CA (N=13)**



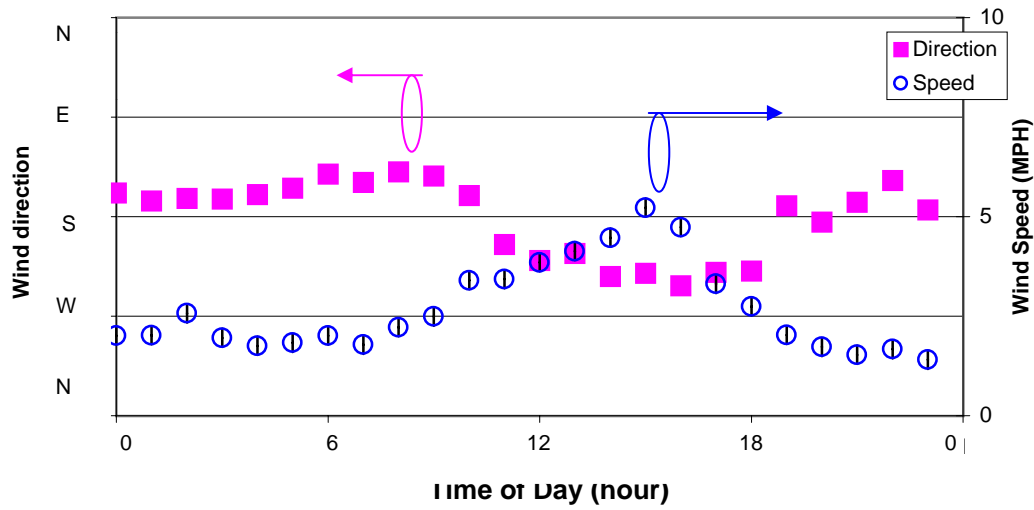
**Fig. 33a. Metal oxide concentrations in coarse PM as a function of time period of the day, Riverside, CA**



**Fig. 33b. Metal oxide concentrations in fine PM as a function of time period of the day, Riverside,CA**



**Fig 34. Wind direction and speed fluctuations during the day;  
Downey (December2000-January 2001)**



**Fig. 35. Wind direction and speed fluctuations during the day;  
Riverside (February-May 2001)**

